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GEORGE REID
Editor

CONTENTS

Finishing Pressure Still Distillates Into Gasoline.....247
W. L. Nelson

Interesting Operating Features in Skelly's Cunningham Plant..251
J. C. Albright

Economies in Doctor Treating.....255
Carl W. Berger

Forward Process Aromatic Fuel.....260
William Kaplan and William E. Forney

Natural Gas as a Chemical Raw Material.....264
I. N. Beall

Oiliness; Its Meaning and Value in Motor Oils—Part I.....269
S. Kyropoulos

The Construction and Operation of Gasoline Plants—Part 3...271
R. L. Huntington

Cleaning High Sulfur Gases.....276
Michael J. Leahy

Utilization of Petroleum Coke.....280
D. Glynn Jones

Gasoline Plant in Fitts Pool Has Operating Problems.....282
J. C. Albright

Departments

The Look Box.....245 and 39a

Plant Activities.....46a

Business Notes.....49a

Ideas.....51a

Science and Technology (Abstracts).....57a

New Equipment for the Modern Plant.....67a

Catalogs and Bulletins.....73a

Advertisers' Index.....74a

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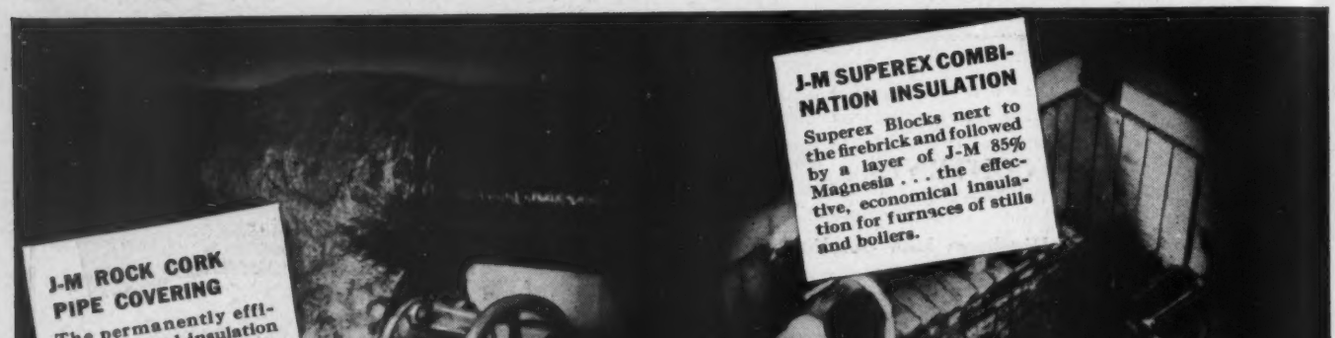
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VOLUME 15, No. 7 JULY, 1936

REFINER
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The Look Box

SHELL OIL COMPANY of California went into the flat, open country out in the center of the San Joaquin Valley, leased a block of 6000 acres and proceeded to make this wildcat create a distinct sensation in California oil circles by getting production at the rate of 800 barrels of 62 gravity oil, and 10,000,000 cubic feet of gas. The field lies between Bakersfield and Taft, a short distance from the highway joining these two California oil centers. Detailed analysis of this new crude is lacking at this time, and the first well may not be adequate to make a guess as to what type of crude lies below the gas cap.

New Crude

The importance of the strike however lies in the fact that the discovery has exploded an old theory about the San Joaquin valley to the effect that the center of the valley was a great syncline where oil would never be found. Now it seems that further exploration of this great valley is in order—and out of this likely may come important additions to California's crude oil reserves.

THE use of the paper container for liquids, ice cream and food products generally has been growing during recent years. Now, in many communities it is reported that the paper container (well paraffined) for dairy products is being popularly accepted. Such a trend, if it can circumvent competitive conditions, politics and other hampering influences, can do much toward creating larger demand for paraffin in addition to becoming an aid to the paper pulp people. Some commentators feel that the possible increased demand for paraffin used in construction is sufficiently great as perhaps to limit the use of the paper container to paraffin production.

Paraffined Containers

It has been remarked that the petroleum industry should not join with paper and fibre and promote the use of the paraffined container, else the dairymen and others may return to the horse and wagon method of delivery. Quite on the contrary, it is claimed by dairymen that the net cost of using such a single-service container is not too high. He maintains, quite logically, that the savings in collection, washing, breakage, and the like, more than offsets the first cost. Not only the dairyman is looking to paper—oil companies are finding paper containers for lubricating oils workable in some instances, likewise greases and other products. Something else to think about.

ALTHOUGH much optimism was generated late last month by the Bureau of Mines estimates of the July demand for crude oil and gasoline, there is danger that this optimism may lead to excesses, particularly in refinery runs to stills. Crude production allowables for July have been set, and they are sufficiently low to indicate that the national output of crude will be held fairly close to federal recommendations. But there is some danger that the prospective increase in demand may induce refiners to process too much oil.

Too Much Gasoline

Gasoline inventories have been so high in recent

months as to cause unsteadiness of the markets, and the aim of refiners in July should be to bring about a substantial reduction of the stocks. The Bureau of Mines in its recommendations for July suggests that the expected heavy consumption of the month should make it practicable to reduce the gasoline stocks approximately 5,000,000 barrels. The crude production quotas are predicated on such a change in the gasoline stocks.

There is some concern that gasoline output will be pushed too high in the months ahead not only by the strong demand for gasoline but also by the fuel oil situation. While California has extensive fuel oil stocks, the inventories east of the Rockies are comparatively low. In anticipation of the opening of the season of large fuel oil consumption about three months from now, these relatively small inventories are being viewed with some apprehension. This situation offers the danger that fuel oil production will be stepped up substantially, and that this accelerated output will bring at the same time an undesirably high production of gasoline. Some economists deprecate the idea of possible fuel oil scarcity, stating that in any event, supplies could be moved from California to the East, if necessary.

Nevertheless, it is not forgotten in the industry that the past winter brought an unusually large demand for fuel oil, and that the available supplies proved comparatively scarce. In fact, refiners found it necessary to make more fuel oil than they originally intended, and it was that increased production that was partially responsible for the building up of the present excessive supply of gasoline.

Improvement

MORE encouraging for the petroleum industry than any of the present promising figures and statistics is the cooperative spirit that prevails within the industry and among the conservation officials of the leading oil producing states. Producers of petroleum and state authorities have cooperated in a sincere move toward the securing of favorable results this month of July. Since this example of teamwork has strengthened the markets it certainly seems possible that such cooperative effort should be extended into the months ahead.

It is comforting that petroleum consumption is running this year at all-time record levels; that the demand is expected to be especially strong in July; that success appears within reach for the month in balancing supply with demand. But it is even more encouraging to feel that the oil producers and state officials are working together; that self restraint is being practiced for the good of the industry; that the various states are putting shoulders to the wheel in a determined effort to get clear of the quagmire of overproduction in which the industry has been laboring for several months. In all this the refining concerns can be more helpful in the future than in the past. If this spirit of cooperation can be maintained, the industry will go through the rest of the year enjoying profitable operations; although a let-down of team work might rapidly bring on a serious break of markets and prices; especially after the summer months, since gasoline inventories are larger than desirable.

Cracking

NOW, as in the past two decades, cracking is essential to profits in modern refinery operations. The cracking process for production of gasoline is the dominating force in the conservation of crude oil, has been, and is so obviously a fact that THE REFINER has made but scant mention of this phase. Much, however, has been written in these columns and published in the technical section of this journal pointing to the necessity for cracking processes on the plant yard and the necessity for keeping those facilities in a stage of almost constant improvement—or of replacing obsolete units with modern equipment which will not only crack but top, reform and crack. And the handwriting on industry's wall does not grow dimmer with passing years.

Consider the facts recently presented by Egloff and Nelson before the Chemical Engineering Congress at the World Power Congress, London. The demand for cracked gasoline has grown so great that during 1935 one-fourth of the total of 217,560,000 barrels of straight-run was cracked or reformed. The same year 205,920,000 gallons of cracked gasoline were produced from a great variety of charging stocks ranging from naphtha, kerosene, gas oil, fuel oil residue and crude itself.

In 1912 (before the advent of commercial cracking) the yield of gasoline from normal distillation of crude was 12 percent. In 1935 the percentage recovery was 45 percent. In 1935, 80 percent of the world's cracking of oils was within the United States where 205,920,000 barrels was produced as against an estimated production of 45,300,000 barrels for the rest of the world.

The investment in cracking units in 1913, according to these authors, was about $2,000,000, whereas in 1936 it was over $400,000,000. And the industry is spending over $5,000,000 yearly in research in the art of cracking.

Cracking at 900° F. to 1100° F. and at pressure up to 1000 pounds per square inch pressure is not a cheap operation. Maintenance costs for this division of refining alone present a sizeable figure. Obsolescence costs are higher. The tech-

(Continued on page 39a)

Centrifuge Room, Acid Treating Plant, Wilshire Oil Company's Refinery, Santa Fe Springs, California.
(Courtesy Stratford Engineering Corporation)

Finishing Pressure-Still Distillate Into Gasoline

W. L. NELSON
Consultant Professor of Petroleum Refining, University of Tulsa

THE common methods of treating pressure distillate for the removal of sulfur, gum, and colored materials, are:

(1) Acid treatment followed by redistillation and a sweetening treatment. The redistillation may be conducted by the use of steam or vacuum.

(2) Treatment in the vapor-phase with fullers earth; sometimes followed by sweetening.

(3) Treatment in the liquid-phase with fullers earth; sometimes followed by sweetening.

(4) The use of inhibitors and dyes. The inhibitor slows down the rate of gum formation and the dye serves to mask the natural yellow color of the product. These alternatives may also be used in conjunction with the aforementioned methods.

The methods are not equally satisfactory for a particular distillate and therein lies the value of an economic comparison of the several methods. However, every distillate has different properties and hence only general material can be presented. In order to use the data, the refiner will need to study his particular pressure distillate in the light of the following discussion. The tables and figures herein given are merely facilities by which the chemical and physical characteristics of the distillate can be evaluated in terms of plant costs.

REDISTILLATION

Acid treating and redistillation has been the most widespread method of finishing pressure distillate and it is still used by many refiners. For most distillates it is a more expensive method than the other

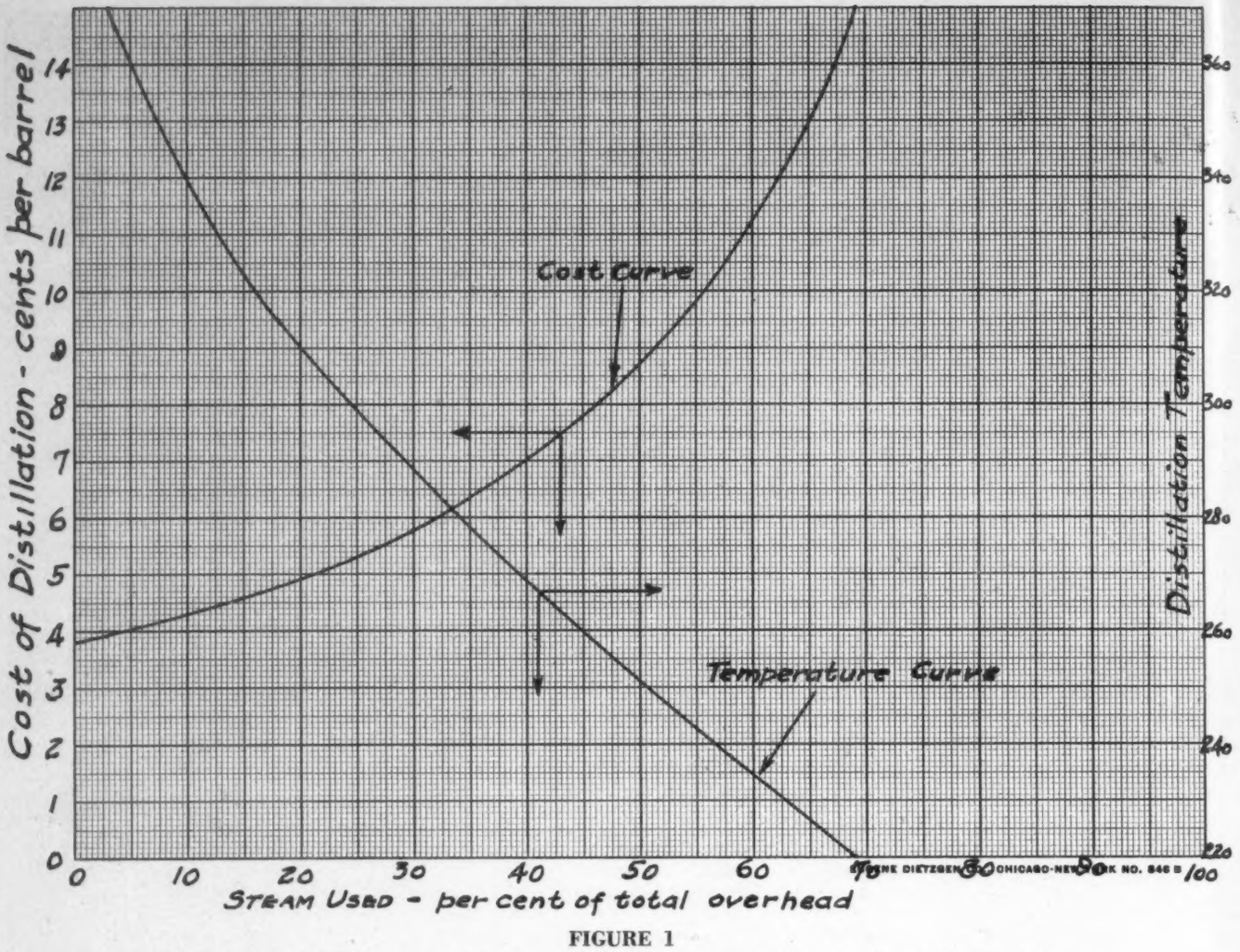


FIGURE 1

Cost of Redistillation and Distillation Temperature as a function of Steam Consumption.

methods that follow but in certain cases a distillate can be handled in no other way.

The amount of steam used during the distillation is an important economic factor. By the use of steam the distillation temperature can be reduced and some refiners are operating at the low temperature of 225° F. The justification that is given for the use of the large amount of steam that is required in distilling at 225° F., is the ease of chemical treatment. One refiner uses only 0.6-0.7 pounds of acid per barrel of pressure distillate but about 350 pounds of steam per barrel of oil is used in the redistillation.

Other refiners believe that a relatively small amount of steam (as little as 15 pounds per barrel) may be effective. They believe that temperature in itself is not important provided the temperature is below the temperature at which decomposition or hydrolysis of the alkyl sulfates occurs. These sulfur compounds are produced during the acid treatment. Although the alkyl sulfates probably do not decompose until a temperature of 375° F. is attained, a lower distillation temperature such as 300° F. may cause decomposition because of localized overheating of part of the material to temperatures exceeding 375° F. even though the temperature of the main bulk of material is at 300° F. Trusty[1] has published the following indication of the effect of steam on the color of the distilled product:

[1] "Acid Treatment of Cracked Distillate . . . " Ref. & Nat. Gaso. Mfg., Aug., 1932, pg. 455.

Percent Steam in Overhead	Color
0	18
5	22
20	25

No published information is available which shows the relation between the amount of acid required and the amount of steam required for distillation. However, for many distillates the use of a light acid treat requires the use of more steam than if a heavy acid treat is employed. Figure 1 indicates the general relation between cost of distillation and temperature of distillation (or steam used).

The cost of acid treatment as a function of the amount of acid used is given in Table 1.

TABLE I
Acid Treating Cost

Pounds Acid per Barrel	DIRECT TREATING COST, CENTS PER BARREL		
	Fixed	Chemicals	Total
1	1	0.7	1.7
2	1	1.4	2.4
3	1	2.1	3.1
4	1	2.8	3.8
6	1	4.2	5.2
8	1	5.6	6.6

The following analysis is a hypothetical case which will indicate how the refiner may use Figure

1 and Table 1. A particular distillate is examined in the laboratory and it is found that the relation between the amount of acid used and the steam for distillation is as follows:

Pounds Used in Acid Treat	Percent of Steam Required
0.8	50 (250° F.)
2	15 (325° F.)
3	10 (340° F.)
8	2 (370° F.)

By interpolating in Figure 1 and Table 1 the following approximate overall costs of treating and distilling are obtained:

Pounds Acid, per Barrel	Cost of Treatment, Cents per Barrel	Cost of Distillation, Cents per Barrel	Total Cost, Cents per Barrel
0.8	1.56	8.7	10.26
2.0	2.4	4.62	7.02*
3.0	3.1	4.33	7.4
8.0	6.6	2.66	9.26

* Very close to the minimum point.

This material is plotted in Figure 2.

For this particular distillate it appears that the use of 1.5 to 2.5 pounds of acid per barrel is the most economical operation. This necessitates the use of 12 to 30 pounds of steam per barrel and a temperature of about 325° F. It is obvious that distillation temperatures below about 300 ° F. are not economical and to approach 250° F. is grossly expensive. In order to use such temperatures some refiners have turned to the use of vacuum distillation. In these plants the lowest boiling part of the distillate (about 50 per cent) is distilled at atmospheric pressure and the remaining part is distilled in vacuum. A maximum temperature of 225-250° F. can be obtained more cheaply by the use of the vacuum than by steam but in many cases a vacuum plant cannot compete with steam plants operating at a temperature of 325 to 350° F. Obviously the decision rests with the particular distillate that is handled.

VAPOR-PHASE TREATING

For low-sulfur-bearing distillates vapor-phase treating is the cheapest way to produce a white gasoline. However, even a cheaper operation is a combination of vapor-phase treatment and the use of an inhibitor. Again such an operation is dependent on a low sulfur content. The economic features of the liquid-phase processes which utilize clay are much the same as for the vapor-phase process.

The cost of vapor-phase treating is a function of the cost of clay, the tons of clay required per barrel of oil and the amount of reburning that is possible. Table 2 is a comparison of the cost of clay treating

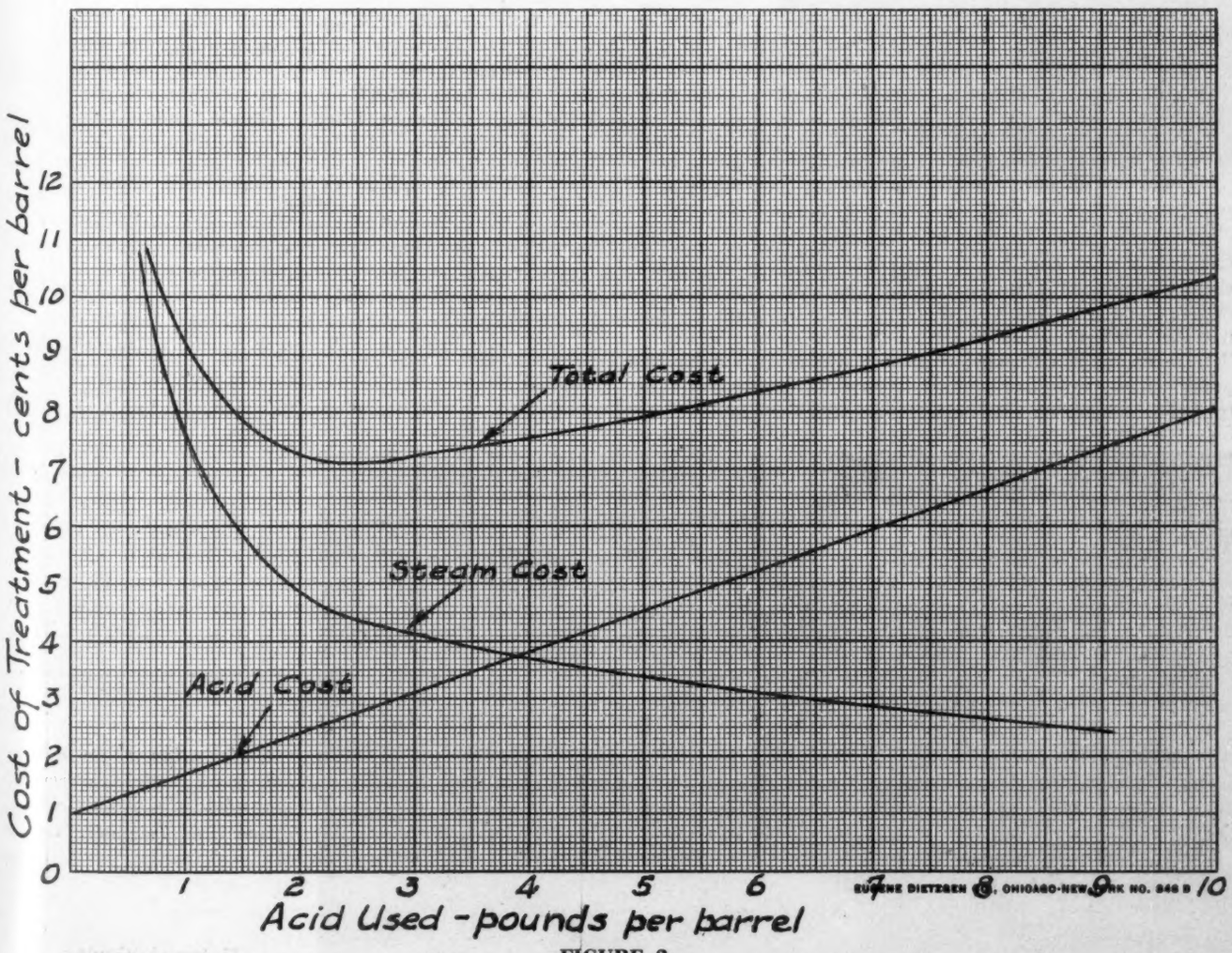


FIGURE 2

Most Economical Amount of Acid to use in Treating and Redistilling Pressure-Still Distillate.

as a function of these variable. Royalty is the main cost in vapor-phase treating.

TABLE II
Cost of Vapor-Phase Treating

Barrels Processed—Per Ton	COST OF TREATING, CENTS PER BARREL				
	Clay Used Once Only		Burning Clay 8 Times		Burning Clay 30 Times
	@ $10 per Ton	@ $20 per Ton	@ $10 per Ton	@ $20 per Ton	@ $15 per Ton
1,000	7.3	8.3	6.7	7.0	6.6
2,000	3.7	4.2	3.4	3.5	3.3
4,000	1.8	2.1	1.7	1.8	1.6
10,000	0.7	0.8	0.7	0.7	0.7
20,000	0.35	0.4	0.35	0.35	0.35

Thus when clay treating can be used it is a highly economical operation. The throughput per ton of clay usually ranges from 3000 to 15,000 barrels in the Gray process and for the liquid-phase clay processes the throughput is less but seldom less than 1000 barrels.

An advantage of the clay processes is the fact that highly unsaturated gasolines such as those from vapor-phase cracking processes can be treated without lowering the octane number to a great extent whereas acid treatment would result in the removal of a large amount of the olefinic hydrocarbons. This factor is not of such great importance with regard to gasolines produced by mixed-phase cracking processes.

USE OF INHIBITORS

The use of inhibitors or antioxidants is a valuable contribution to our methods of finishing cracked gasolines. These materials delay the formation of gum to such an extent that in many cases acid treatment can be dispensed with. The usual inhibitors do not improve the color of the product and hence the gasoline must either be colored by means of a dye or be subjected to a preliminary light acid treatment for the improvement of color.

In those cases in which only an inhibitor is used, the method is highly economical and the aforementioned methods usually cannot compete. Table 3 indicates the relatively low cost of treatment by the use of inhibitors.

The expense of using inhibitors amounts to little more than the cost of the chemical itself and the laboratory control costs, because the mixing of the oil and chemical involves little cost.

TABLE III
Cost of Inhibitors, Cents per Barrel of Gasoline Treated*

Chemical Required, Pounds per 1,000 Barrels	COST OF ANTIOXIDANT, DOLLARS PER POUND				
	0.35	1.25	1.35	2.00	3.00
1	.035	.125	.135	.20	.30
2	.07	.25	.27	.40	.60
4	.14	.5	.54	.80	1.20
6	.21	.75	.81	1.20	1.80
8	.28	1.0	1.08	1.60	2.40
10	.35	1.25	1.35	2.00	3.00
12	.42	1.5	1.62	2.40	3.60
15	.525	1.875	2.025	3.00	4.50
20	.70	2.5	2.7	4.00	6.00

* E. I. du Pont de Nemours & Company—Tech. Bull. No. 4, page 8.

Table 4 is an indication of the amount of each inhibitor that is being used and the approximate cost of each. However, the susceptibility of various gasolines to a given inhibitor is not a fixed relationship. In other words, one inhibitor may be excellent for a given gasoline, whereas other inhibitors may be more suitable for other gasolines. Again the refiner is confronted with the fact that all stocks are different and that a laboratory examination must be conducted on any particular stock if entirely trustworthy results are to be obtained.

TABLE IV.
Cost and Amount of Inhibitor Required.

MATERIAL	Approximate Cost, Dollars per Pound	Amount Used, Pounds per 1,000 Barrels
(1) Monobenzyl-para-aminophenol	3.00	2.6— 7.9
(2) Para-hydroxyphenylmorpholine	2.00	4.0—10.5
(3) Du Pont—No. 2 (Tributylamine)	1.20	5.0—10.5
(4) Dibenzyl-para-aminophenol	1.35	5.3—13.1
(5) Du Pont—No. 3 (Solution of 1)	1.55	5 —16
(6) Alpha Naphthol	.60	6.8—22.2
(7) Du Pont—No. 4 (Solution of 4)	.38	26 —65

In conclusion, Table 5 is a comparison of the range of cost for the different methods of treating.

TABLE V.
Comparison of Treating Cost.

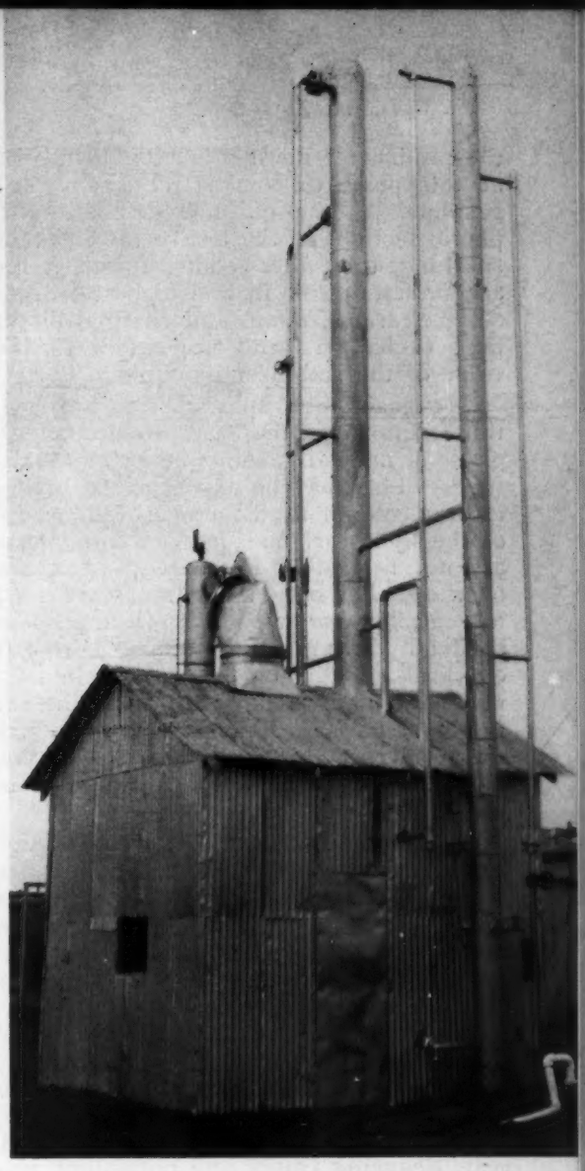
METHOD	Cost, Cents per Barrel	Notes
Acid and steam (350° F.)	6— 9	White gasoline
Acid and steam (250° F.)	10—14	White gasoline
Acid and vacuum (225° F.)	6—10	White gasoline
Clay vapor-phase	0.8— 4	White gasoline
Clay liquid-phase	1— 8	Colored gasoline
Inhibitors	1— 4	Colored gasoline

Refrigeration room operating in conjunction with Stratford Contactor-Centrifuge Cold Treating Plant.

Photographs Courtesy
Stratford Engineering Corp.

Interesting Operating Features In Skelley's Cunningham Plant

J. C. ALBRIGHT



High pressure absorbers used in Skelly Oil Company's gasoline plant at Cunningham, Kansas. Absorbers operate at 1400 pounds pressure.

SKELLY OIL COMPANY'S gasoline plant, located a mile north and a mile west of Cunningham, Kansas, processes four types of gas. The wells in that area are sweet on one side and slightly sour on the other. High-pressure gas is processed before it is used to flow and repressure the productive zones from which oil is lifted, and the other type of gas is that coming from the wells produced by gas lift. The sour gas is only slightly so, and does not show when blended with the sweet gas. However it passes separately through one absorber while all other gas except the high-pressure gas in its initial stage is processed through another column. High-pressure gas is received from the wells and passes through the two high-pressure absorbers at 1400 pounds.

The plant is considered a well-pressure unit, as all gas passes through the various absorbers at the pressure furnished by the flowing wells. All of the gas, high- and low-pressure, is sufficiently low in temperature that it is not necessary to pass it through cooling unit, and therefore, it passes from the plant intake headers directly to the absorbers where it is stripped of its desired gasoline fractions. An oil-to-gas ratio of 40 gallons per thousand cubic feet is circulated in the low-pressure absorbers, which are maintained at 40 pounds, gauge, and approximately 5 gallons per 1000 cubic feet in the absorbers operated at the higher pressure. The lean oil is circulated through the low-pressure absorbers by electric motor-driven centrifugal pumps and through the high-pressure columns by an outside piston-packed steam pump, both taking suction from a common line. To prevent the high-pressure discharge from backing up into the suction, a horizontal check is installed on the pipe line leading from the high-pressure pump, with fittings manufactured to operate at 2000 pounds.

A single building houses the low- and high-pressure oil pumps, but the high-pressure absorbers are set in a different part of the yard, and removed some distance from the low-pressure units. Because of the small amount of oil circulated, small lines are attached to each of the two high pressure columns leading to the top. Only one liquid-level control unit is used for both columns, as the two are connected at the base by an equalizer line. Two thousand-pound working pressure valves and fittings are installed on these columns, and special float cages control the fluid level in the base of the absorbers. The float arm operates on a remote control attached at the other end of the tubing to a high-pressure ½-inch controlled valve with high pressure block valves on both sides so it can be removed if necessary.

These columns were built especially for use in this plant, and a high pressure residue scrubber was placed on the outlet of the residue gas as a common vessel for both absorbers. The scrubber is equipped with a specially built float cage to trap out oil which might carry over with the residue gas. This operates similarly to the one on the absorbers, and traps the oil into the rich oil line leading to the distillation unit.

The rich oil is processed in a still which has a combination of evaporating and dephlegmating units incorporated in one column. Reflux pumped back over the column is used to control the end point of

the product of distillation, but no attempt is made at this point to control the vapor tension of the gasoline. As the gasoline is condensed in atmospheric sections in the louvre tower, or more strictly speaking, the water-cooling tower, it returns to an accumulator tank from which it is removed by a close clearance pump and charged directly through heat exchangers and preheaters to the top inlet valve of the stabilizer manifold.

The gasoline is split up into two major cuts in this fractionator, the base product being the regular grade of natural gasoline being manufactured at the time—which may be any specified grade by balancing the column—and the overhead, a butane cut. All of the hydrocarbons removed from the charge that are not needed in the base product are taken off overhead, but only the butanes are recovered as a top cut. The major portion of the propane and other lighter hydrocarbons are removed from the liquefied overhead product by evaporation in the condensate receiver, and are removed through lines to the boiler fuel system. The liquefied gases are trapped from the receiver to high-pressure storage tanks set outside the plant yard a safe distance from the other units.

Considerable work and experimentation has been, and is still being carried on in the plant, and the various oil fields in Kansas to determine the best method and the most efficient equipment for the use of butanes for engine fuel. One of the Cunningham gasoline plant's light delivery pick-up automobiles is being converted so this fuel can be used. A fuel tank was made at the plant which holds approximately 15 gallons of propane under a working pressure of 100 pounds. Specially manufactured valves and fittings were installed on the tank which was placed in the pick-up body just behind the driver's seat. Reducing valves and regulators, heat exchangers and a carburetor, or gas fuel unit, were installed on the car which replaces the original liquid fuel equipment. Good results have been reported when using butane as a fuel for drilling wells in Northern Kansas where natural gas is not readily obtained. Butanes are shipped from the Cunningham gasoline plant to the fields near Russel, Kansas, and other points, and a specially equipped truck is making frequent trips with this product.

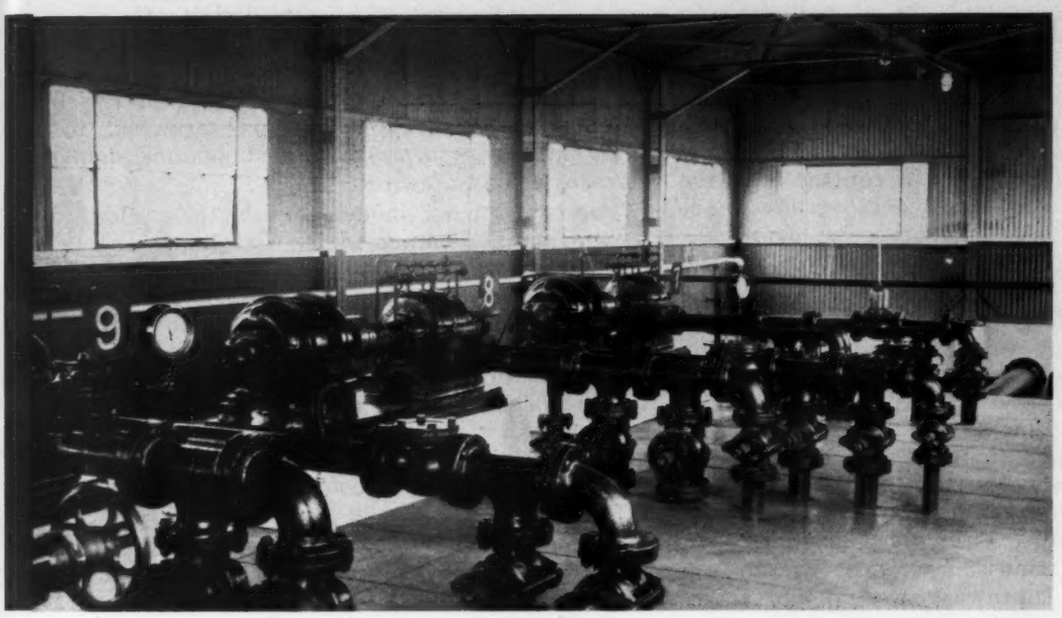
The stripped high-pressure gas which leaves the top of the two high pressure absorbers and the after-scrubber is carried to an additional scrubber set on the residue line where it connects to the high-pressure field line. This scrubber is automatic in action, so far as trapped liquid is concerned. It is equipped with a mist extracting unit to prevent any liquids from entering the high pressure field line. An instrument on the side of this scrubber controls a liquid outlet valve through which oil is trapped back to the plant absorption system.

The residue gas removed from the top of the absorbers is passed through a master back-pressure regulator which is set to maintain the desired working pressure on the columns. Gas passing from this master regulator enters a header containing two additional regulators, one of which permits gas to flow to the residue stack outside the plant fence. The second regulator permits the regular flow of residue to enter the intake header of the gas engine-driven compressors. A third connection on this header, all of which are above the ground level, is where fuel gas for engine consumption and for boiler fuel make-up is removed. The regulator placed on the emergency vent line is set at a working pressure above both the master regulator and the one serving the intake of the compressors and operates only when the flow of gas exceeds the capacity of the compressors, or when trouble develops in delivery of gas to the transportation system.

Fuel for the boiler battery is taken from the vent line on the fractionator overhead accumulator tank, and make-up fuel is taken from the line on the residue header to supplement any deficiency at the fractionator unit. A regulating valve placed at the junction of these two lines prevents propane and other fractionator vapors from passing to the residue system at the absorber scrubbers. When the pressure on the fractionator vapor line is less than that on the residue-gas line, the regulator opens to allow gas to pass to the boiler-fuel system.

Gas taken to the fuel header serving the eight twin gas engine-driven compressors is further reduced

Layout of compressor control gates which are set in floor to facilitate switching of gas by operators without leaving building.



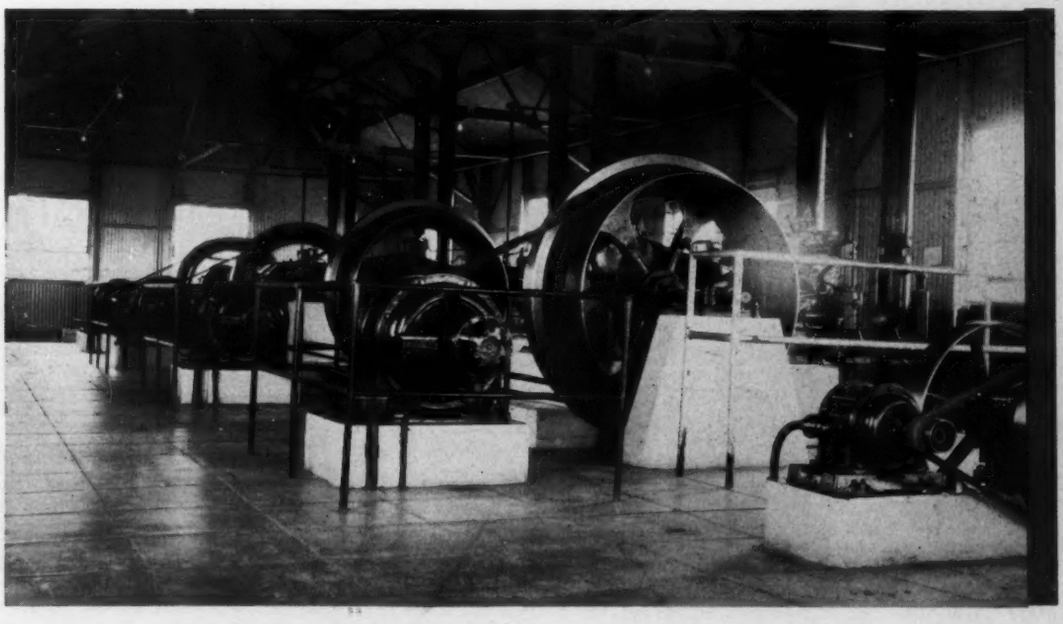
Low pressure oil circulating pumps in Skelly's Cunningham gasoline plant in Western Kansas.

through a twin regulator setting composed of two identical regulators operating in parallel. Each regulator takes gas from a common line and passes it at reduced pressure to a common fuel header. This installation is at a point about midway of the engine room instead of one regulator at each end of the fuel header. The combination of the two regulators on a common setting operating in parallel provides a more even flow of fuel to the gas injection heads of the engines.

The engine room, while not primarily a necessary feature of this plant, is connected to, and operates on, the residue gas flowing from the low-pressure absorbers to boost it through two stages to the gas line running nearby. These engines are equipped with pressure injection firing heads and have the cylinders inverted so the exhaust leads through the roof instead of the older type of underground lines. To facilitate control, starting and shutting down of the engines, all suction and discharge valves are placed inside the building, but beneath the concrete floor. All but the packing glands are covered, with the wheel just above the floor. In this section of the country, where the wind blows consistently, this is said to be favorable for efficient operation and prevents opening and shutting of doors when it is necessary to shut down or start an engine.

The auxiliary power room which is attached to the gasoline plant, contains four twin-cylindered four-cycle gas engines driving generators to supply the plant with current for motor operation. The oil field nearby also operates many motor-driven pumps and other units and derives its power from this room also. The combination water circulating system which affords jacket cooling for all gas engines in the plant yard is located in the auxiliary engine room. Two motor-driven centrifugal pumps are used to pick the water from an underground sump and pass it back to the cooling tower.

Water produced in this area from subsurface sands and gravels is comparatively soft, containing approximately three to four grains of permanent hardness. Boiler-feed water is used as it comes from the wells, but the jacket water is carried in an enclosed sys-



Generating room in Skelly Oil Company's Cunningham gasoline plant, used to generate electricity for plant motors, plant lighting and field operation where electricity is required.

tem to prevent contamination from drifting sand and vegetation. The water runs by gravity over the compressor and power cylinders from a pair of 1600-barrel wood tanks, but is forced from the sumps to the atmospheric cooling coils placed in the water cooling tower. The tanks are covered and the only time the water comes in contact with the air is when it falls from the jacket overflow pipes to the lines leading to the underground sumps.

A constant head is maintained at all times upon the discharge of the centrifugal pumps pulling the water from the underground sumps through the operation of a "kidney valve" placed in the pump room. This float valve and cage is placed above the pump floor and controls a valve placed in the discharge line from the pumps to the cooling coils. The level of the water in the underground sump actuates the float arm of this unit, and prevents the centrifugal pumps from removing all the water from the sump and becoming airbound.

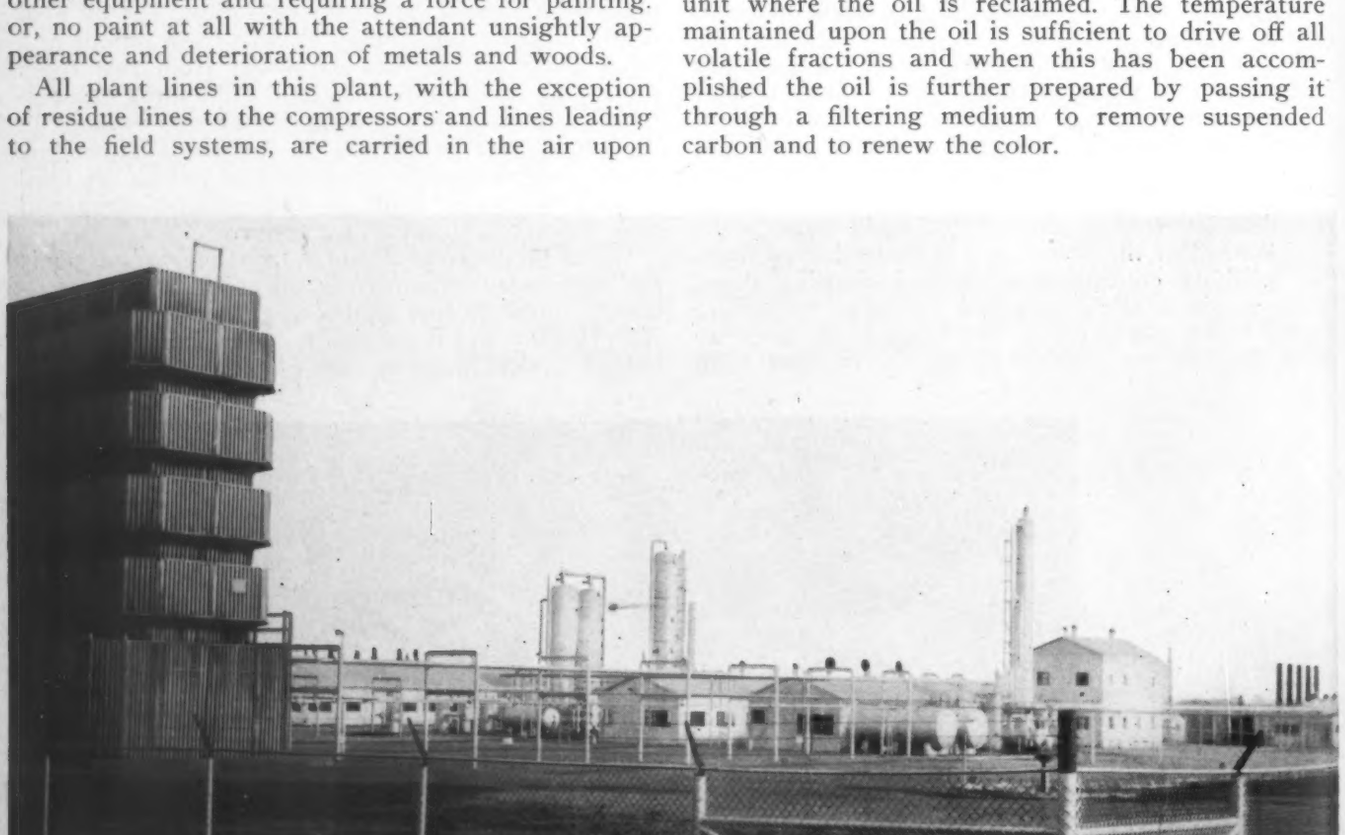
As the prevailing winds in western Kansas are from the south and southwest, the cooling tower was located in the northwest corner of the yard so mist and spray will not fall upon the painted surfaces and insulation of the equipment damaging the appearance and causing corrosion. All too often little regard has been given this feature of plant planning and cooling towers have been placed on the windward side of the plant, and with the older type cooling tower, large amounts of water lost due to high wind velocity has fallen upon the buildings and other equipment and requiring a force for painting. or, no paint at all with the attendant unsightly appearance and deterioration of metals and woods.

All plant lines in this plant, with the exception of residue lines to the compressors and lines leading to the field systems, are carried in the air upon steel stanchions, high enough that trucks can pass beneath them. Corrosion due to adverse soil conditions is completely eliminated by this method. With adequate swings or expansion joints in the lines, coupled with moveable supports attached to the lines and cross arms of the stanchions damaging stresses are avoided.

For convenience in designating the various units in the plant, whether in the gasoline plant or the engine rooms, all pumps and gas engines are numbered and are identified by having large metal placards attached to same portion of the unit. When the superintendent desires that work be done on a certain unit, such as repacking, adjusting or timing, he needs only to give detailed instructions regarding the type of repair to be accomplished together with the unit number. This feature prevents misunderstanding and also facilitates reports coming in from the plant to the office.

When servicing the compressors and power engines with lubricating oil, the oiler draws the lubricant from an underground tank through a service cock. The tank holds a large amount of oil which may be replenished by truck tank. Air pressure maintained on it while in service prevents the waste usually encountered when oil is drawn from drums placed in the engine rooms.

At regular intervals the crank case oil is withdrawn from the engines and replenished with a fresh charge. The old oil is taken to a part of the plant equipped wtih a gas-fired steam-distillation unit where the oil is reclaimed. The temperature maintained upon the oil is sufficient to drive off all volatile fractions and when this has been accomplished the oil is further prepared by passing it through a filtering medium to remove suspended carbon and to renew the color.



Skelly Oil Company's Cunningham, Kansas, gasoline plant.

Economies in Doctor Treating

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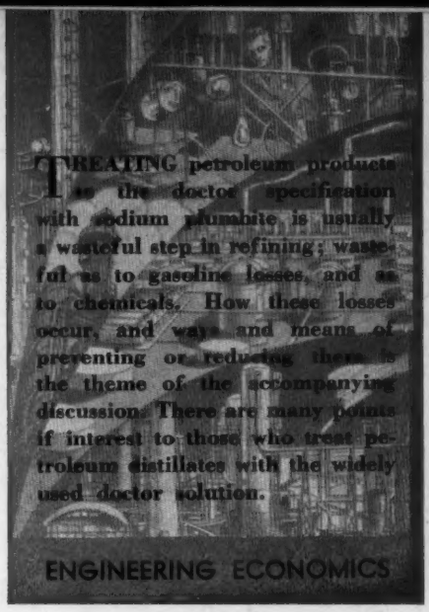

TREATING petroleum products to the doctor specification with sodium plumbite is usually a wasteful step in refining; wasteful as to gasoline losses, and as to chemicals. How these losses occur, and ways and means of preventing or reducing them, is the theme of the accompanying discussion. There are many points of interest to those who treat petroleum distillates with the widely used doctor solution.

CONSIDER a typical plumbite sweetening plant. This plant treats gasoline by means of a solution of litharge in caustic soda, either by batches or by continuous treaters. When the batch has been sweetened, or when the doctor solution in the continuous treater has lost its strength through the conversion of sodium plumbite to lead sulphide, the spent chemical is drawn off, together with as much of the blackstrap emulsion as possible, into recovery tanks where it is heated to 160-200° F. with steam, and blown with air. By this process, the lead sulphide is converted into lead sulphate by oxidation, and the latter redissolves into the caustic soda as regenerated sodium plumbite.

On the face of the question, the above seems to be a simple, expedient, and economical procedure; one by which the same chemical may be used over and over again. Of course, this cycle cannot go on indefinitely for the reason that the original caustic soda is gradually transformed into sodium thiosulphate, sodium sulphate, etc., as side reactions of the conversion of lead sulphate into sodium plumbite, and also for the reason that mechanical losses of lead and caustic occur in the system. The magnitude of these losses and other losses with which they are closely associated, is interesting from a financial standpoint. Visualization of good American dollars slipping down the sewer and evaporating into the atmosphere may even be alarming as well as interesting.

Most of these losses can be listed under the headings of carryover and evaporation.

CARRYOVER

After a batch of gasoline, kerosene, etc., has been sweetened and the doctor drawn off, varying percentages of lead sulphide and doctor solution remain in the agitator, suspended in the oil or clinging to the walls or the cone. During the water wash or light caustic wash that follows, most of this material is drawn into the sewer (along with some of the oil) and is lost.

At least two simple methods of reducing such losses are available. First, the batches can be drawn down more closely during the doctor draw-off. Drawing by increments, with a period of settling between each draw-off is effective. In this manner, more of the lead sulphide and doctor solution finds it way back to the recovery tank. This method can be used only when there is some means of economically recovering the large quantities of oil drawn off with the doctor. Such means will be discussed later. Another method of recovering these carryover, or drawoff losses is suggested; that of providing a suitable system of traps for the lead sulphide and oil that find their way into the sewer. Such a trap system will be described later.

If the continuous treating system is used, carryover losses can be controlled in the manner already mentioned, and by other methods. In the first place, carryover is caused either by improper mixing and settling equipment or by improper treatment. It is obvious that should the mixing of doctor and lead sulphide, etc., be so turbulent that provisions for the necessary settling time are inadequate carryover of doctor, gasoline, and lead sulphide into the water wash (and sewer) or into the emerging treated stream, will follow. By improper treatment is meant any handling that fails to give a clean, fast settling, "break." Carryover often occurs between the time that the treater is started up and the time that the operator gets his chemicals so apportioned and adjusted that a good "break" results. The most important factor in the adjustment mentioned is the addition of sulphur to oxidize the lead mercaptides to the corresponding disulphides and precipitate the lead as lead sulphide. It has been found good practice in this connection, to add a small excess of sulphur, rather than an insufficient amount for the period of time (usually about 15 minutes) that occurs before the operator gets his chemicals properly adjusted. This procedure insures a clean "break" at the inception of the treatment. Other precautions might be mentioned such as prevention of gasoline losses in the water wash by proper settling, and control of water levels in the wash drums. Still another is to take the doctor solution off the treater before it loses its strength completely, thus preventing carryover at the end of the cycle.

There is one method of handling treatment on a continuous sweetening system that has several advantages, and which is but a simple modification of the usual recirculation system. This method has been proven, by trial, under the writer's supervision, on four different gasolines with marked reduction in evaporation loss and carryover in comparison with the usual method.

This system of treatment does not place a given amount of regenerated doctor solution in the treater and then circulate it with incoming gasoline until it is spent. Instead, a full tank of regenerated doctor solution is prepared, and taking suction directly from this tank, the doctor is fed into the system with the

incoming gasoline. The doctor is not recirculated, and accumulates in the settling towers of the treater. At first glance, it would seem that the treater would soon fill with partly spent doctor solution and that, were much gasoline treated, a large amount of doctor solution would need be kept on hand to supply the treaters.

As a matter of fact, however, by supplying fresh doctor continuously, only a small amount need be contacted with the gasoline for the desired sweetening effect. As little as 1 percent of doctor solution to 99 percent by volume of gasoline is usually sufficient under optimum conditions, so that in reality, there is less handling and regeneration of doctor than in the usual system. A few of the benefits of the method are immediately obvious:

a. Less steam consumption and wear on doctor circulation pumps.

b. Eliminates shutdowns for the purpose of "changing doctor."

c. Since the doctor charged is always the same strength, and not gradually weakened by constant recirculation, the other treating conditions such as amount of sulphur added, can be held constant.

d. Since no lead sulphide is being recirculated, emulsion and carryover are lessened.

e. Treater can be run at full speed continuously because there is no necessity for continually increasing the doctor-gasoline ratio.

One disadvantage is that ordinary doctor circulating pumps cannot be run slowly enough to pump the minimum of doctor solution necessary. On new installations, this can be taken care of, and in old plants, the problem can be handled by tying the suction and discharge of the doctor circulation pumps together with the necessary stop cocks so that more doctor is handled by the pumps than actually is discharged by them. In other words, a portion of the pump discharge goes back into the suction, while the actual discharge to the treater is pinched down.

Further, with this system, another pump should be used to pump accumulated doctor in the treaters back to the regeneration tanks. This will allow the treater to run 24 hours per day without shutdown if desired, even on very "sour" gasolines.

Of course, as much lead sulphide is formed with this method as in any other, but it has ample time to settle in the treater and is not continuously being churned with more gasoline with the result, on the system mentioned, that less stable emulsions are formed and less gasoline lost by evaporation.

There is another point that should be mentioned, a point that is very important in diminishing carry-over, but one which a great many treating engineers have overlooked. The point is that on a good many gasolines (and kerosenes) a very much better "break" is obtained if the necessary sulphur is added first to the gasoline before contacting it with doctor solution —not afterward. Apparently the procedure for testing a gasoline to determine whether or not it is sour, i.e., adding doctor solution and gasoline, shaking, then adding a pinch of sulphur and again shaking, has led many to believe that this procedure should be duplicated without question in the sweetening plant. As a matter of fact, some gasolines and kerosenes cannot be "broken" by this procedure at all, and although the gasoline will be sweet, it carries a fine brownish scum which can be removed only by prolonged water washing or filtering.

We will not go into the chemistry of the formation of basic lead mercaptides in the absence of sulphur. It is sufficient to point out that this and similar reactions have been the cause of much grief on the part of some treaters who did not realize the significance but who noted the results of such phenomena. Not only is trouble encountered, but worse, carryover losses are increased. It is suggested to the interested reader that he try a "hand sample" on his gasolines if he is having carryover trouble and if it is apparent that pretreatment with sulphur is advantageous, that he try it on the treating plant. On continuous treaters, insert the sulphur stream behind a pressure-reducing valve or orifice and far enough ahead of the doctor solution to provide good distribution of the sulphur. On the batch agitator, sulphur can be added slowly while circulating or blowing the batch of gasoline or kerosene, the treater taking out samples occasionally and shaking them with doctor solution to determine whether enough sulphur has yet been added. It is good practice to stop sulphur addition before the necessary total has been reached, then to pump on the doctor solution and either blow sweet or add the finishing increments of sulphur.

The writer has studied several systems for the recovery of lead sulphide and gasoline carryover. Probably the most efficient consisted of a system of traps and settling tanks which served the dual purpose of recovering the lead sulphide and improving the condition of the waste water released from the plant. It is always best, of course, to prevent carryover rather than to make provisions for recovering the lead and gasoline, but the system will be described for the reason that in some cases carryover is present in spite of careful handling.

Black strap ordinarily exists in two forms, one which is much heavier than the other. Suspended in slowly moving water, part of the black strap will fall to the bottom of the container and part float on top. It is simply a matter of particle size and degree of emulsification with gasoline and air. To be effective, any trap for the purpose of removing and reclaiming black strap must then have provisions for picking up the lead sulphide emulsion floating on top of the water, and for that which sinks. Semicircular troughs set perpendicular to the flow of the water and dipping just underneath the surface will pick up the oil and the light sulphide, while "mudhog" pumps can pick up the heavier sulphide from the bottom of the trap when the trap is drained. For the latter reason, the traps should be built in parallel pairs so that the flow can be switched from one to the other for cleaning operations.

The light black strap together with the oil can be continuously pumped from the troughs to a separating tank A, Figure 1. Water picked up with the gasoline and emulsion can be drawn off steadily back into the trap. The accumulating oil and lead sulphide can pass conveniently by gravity to tank B, a larger tank, allowing additional settling and separation time. The latter can be hastened by the addition of emulsion breakers. Heavy black strap from the trap bottom can also be pumped to tank B intermittently. In tank B, gasoline (naphtha, etc.) rises to the top of the emulsion and can be pumped away to storage. Taking suction from near the bottom of tank B the stable black strap is pumped to tank C where it can either be steamed to remove the gasoline or fed into a centrifuge for the same purpose. The recovered lead sulphide itself is then added in increments to doctor solution being regenerated.

Such a system as described has been shown to be practical by use for the recovery of doctor carryover and prevention of waste water pollution. A rough sketch of the plan is given in Figure 1.

EVAPORATION

If one were to examine that intimate mixture of lead sulphide, caustic, and gasoline (or other petroleum distillate) that is commonly known as black strap, he would find that an average composition would show in the neighborhood of 45 percent gasoline, 43 percent spent doctor solution, and 12 percent lead sulphide. When writing of the typical recovery operation, it was stated that the black strap along with spent doctor, and perhaps still more gasoline, were all pumped to a recovery tank, heated with steam and blown with air. A natural inquiry arises concerning what becomes of this entrained gasoline and the answer is that usually all of it is lost by evaporation into the atmosphere. If this gasoline is not entirely dissipated, the emulsion remains and the lead does not all go into solution. Furthermore, heavy, off-color gasoline ends remain in the recovered doctor and will discolor the fresh gasoline being treated. For these reasons, the operator is interested in getting rid of the gasoline, but from the economy standpoint we are interested in the extent of and the prevention of these same losses of gasoline. A reasonably accurate estimate, based on actual data from the doctor treatment of gasolines from several sources, would be that for every 1000 barrels of gasoline treated, from 170 to 200 gallons of black strap are formed. From the stated average analysis of black strap (45 percent gasoline), it follows that for each 1000 barrels of gasoline treated, approximately 80 gallons of gasoline would be lost by steaming the spent doctor. For a refinery of average size treating around 200,000 barrels of gasoline per month, this seemingly small item alone would amount to around $10,000 per year. Further, this figure does not

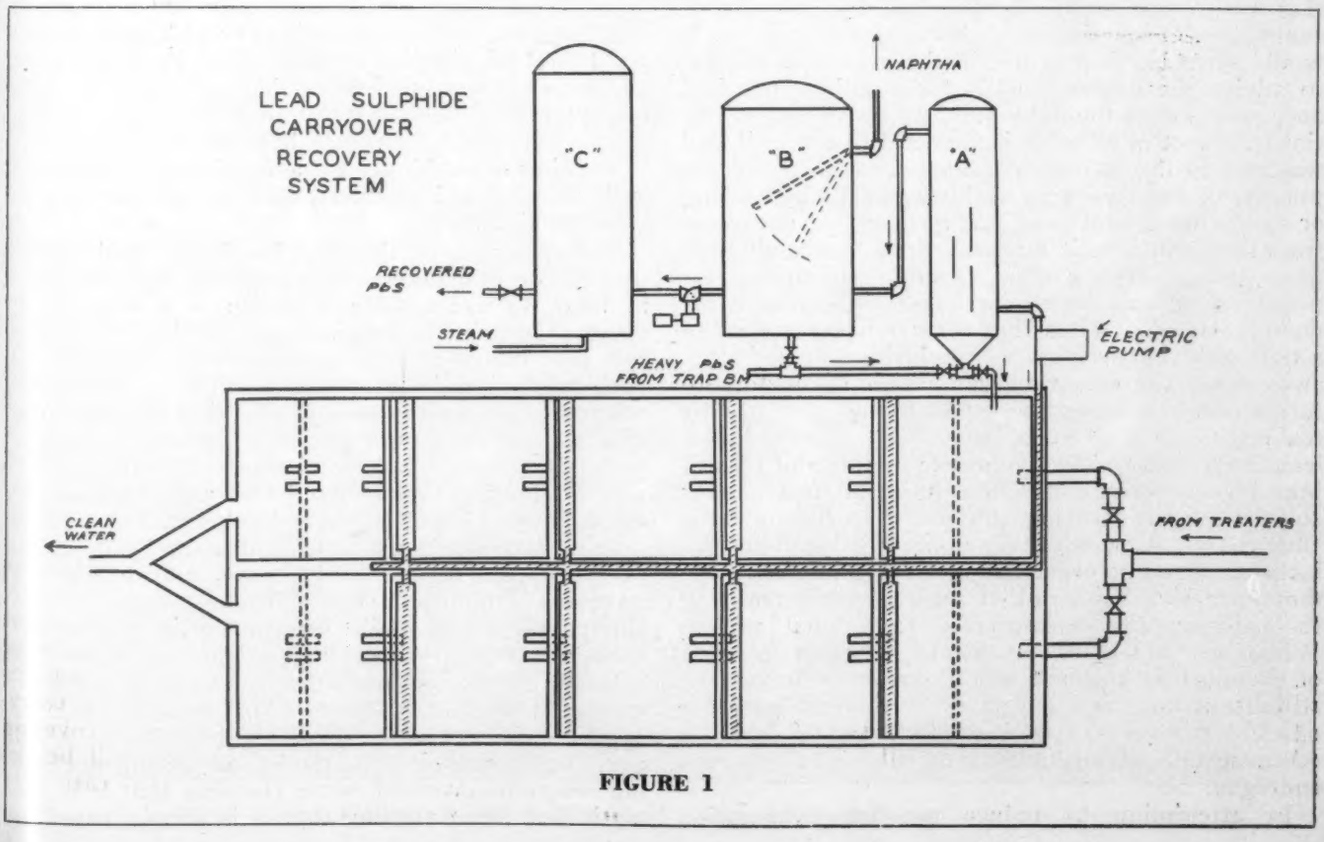

FIGURE 1

take account of un-emulsified oil drawn to the recovery tanks along with the spent doctor and black strap, it being considered possible to settle and draw off this material whether or not this step is routine procedure in any plant under consideration.

That the gasoline losses arising from plumbite sweetening are actually higher than the conservative estimations in the preceding paragraph is fairly well known. Stagner[1] states that from 0.21 to 0.42 gallons are lost from each barrel treated, these figures averaging nearly four times the amounts given above. What is surprising is not that these losses are so great but that the average refiner has permitted this waste to continue for so long.

It might also be pointed out that the steam used to evaporate off emulsified oils in the recovery tanks can likewise be considered largely waste. It is used expressly for the purpose of driving off the oil and breaking the emulsion, requiring temperatures in the neighborhood of 180° F., whereas the oxidation and solution of the free lead sulphide could be carried out quite easily at temperatures at least 50° F. below that mentioned. Since there is a great deal of variation in the manner in which different refineries handle their steam, it is almost impossible to estimate the yearly monetary loss from steam wasted in this manner, but it is safe to say that for the average refinery, it would run into four figures.

Since these evaporation losses from plumbite sweetening arises from the fact that the oil becomes emulsified with lead sulphide and caustic soda, the remedy could take two directions, viz. prevention of the formation of stable emulsions, and for economical methods of separating the emulsion already formed.

The deleterious effects of too-turbulent mixing of doctor solution and gasoline, of inadequate settling time, and of improper operation of the treater have already been discussed. All of the above lead to emulsion troubles. Likewise it should be mentioned that the presence in the doctor solution of heavy concentrations of inactive salts also causes emulsions. It would seem harsh practice, in the eyes of economy, to advise the disposal of doctor solution that had been used long enough to build up heavy concentrations of inactive salts. It is wasteful to retain it and wasteful to throw it away. The solution lies in the practice of first removing usable lead salts by settling or centrifuging and then the recovery of chemicals from the spent caustic for marketing. Newcomb[2] suggests using spent caustic (sodium sulphides) for precipitating and recovering residual lead in spent doctor. He also states that some refiners are using a thorough caustic wash on cracked gasolines before sweetening to reduce contamination of doctor solutions, by removing the gum-forming and trouble making phenols as carbolates. Valentine and Mclean[3] have outlined two complete methods of removing and recovering valuable salts from spent doctor solutions, one involving the use of carbon dioxide (flue gas), and the other of sulphur dioxide. The very fact that doctor solutions are receiving more attention than formerly, indicates that the industry is realizing that therein lies a source of additional profits. Whether or not it is economical to attempt recovery of chemical by-products of the doctor cycle may be still disputable, but it is certainly not questioned that efficient recovery of lead sulphide and gasoline is economically highly important and is to be encouraged.

In attempting to reduce gasoline evaporation losses, we had the alternative of finding an economical method of separating black strap emulsions already formed. There is no question but that gasoline can be separated from the caustic-lead sulphide mixture with nearly 100 percent efficiency by the use of properly designed centrifuging equipment. Use of centrifuging systems have met with variable successes in the refining industry. Poor results can usually be traced not to the theory but to the practice. To be effective, the system must provide a positive means of removing the oily hydrocarbons from the spent doctor in toto, followed by a low temperature oxidation of the lead sulphide into sodium plumbite. Through the removal of gasoline by centrifuging, the gasoline is recovered, the emulsion is broken, and the lead sulphide is set free to be oxidized. Gasoline losses by evaporation are eliminated, the fire hazards attending its evaporation disappear, the doctor solution is kept clean of off-colored gummy residues, and unrecoverable sludge is no longer found in the bottom of the doctor recovery tanks.

Lead sulphide, freed of its surrounding layers of organic residues can be dissolved readily and more quickly in caustic for regeneration and at temperatures of the order of 80° to 125° F. A micro-photograph of a sample of black strap is shown (Figure 2) to give the reader an insight as to the oily, gummy, layers ordinarily surrounding particles of lead sulphide. Low temperature regeneration reduces steam consumption to a minimum, thus involving another economical factor. Further, such a system allows more practical handling of the regeneration. With the emulsion gone, the oxidation can be carried out mechanically with provisions for more intimate mixing of the chemicals with air in the form of a fine mist, all of this without danger of "boiling over" the doctor tank as was easily possible in the old steam and compressed air system. The writer has gone to considerable length in investigating one such system of handling spent doctor[4] and does not hesitate to say that he is satisfied a savings of at least one cent per barrel of gasoline treated could be realized on anything but nearly sweet crude by substituting such a system for the old wasteful method of regenerating doctor. Since the difference between profit and loss in refining often hinges on a fraction of a cent per gallon of finished products, such savings are not to be discredited.

The entire paper, thus far, has been based on the assumption that refiners will continue, for some time at least, to use sodium plumbite as a sweetening agent. One should not, however, lose sight of the fact that this is not the only method of sweetening both cracked and straightrun distillates. There are other methods of sweetening that do not have some of the disadvantages of sodium plumbite, both as to economy of operation and to quality of finished product. Stagner[1] has described the advantages of sweetening with alcholic caustic and sulphur. The method described avoids emulsion difficulties and consequent carryover and evaporation losses, and completely sweetens without the use of lead. It must be considered when one speaks of economy in sweetening.

Some plants are operating on the so-called "lead sulphide" form of treatment, in which gasoline is contacted with a suspension of lead sulphide in caustic soda, and in the presence of air. There is still argument concerning the mechanism of the sweetening reactions involved, some claiming that it is catalytic and some arguing that it is simply based on

slow, continuous oxidation of the lead sulphide to reactive sodium plumbite in the presence of air and caustic soda. The formation of less than the normal amount of disulphides by this treatment indicates that actually both schools of thought are partially correct. By this system, reclamation of lead sulphide, with its attendant losses, is virtually eliminated, but the necessity for reclaiming liquifiable petroleum gases from the air used is substituted. There are further questions such as formation of gum-producing perioxides in unstable gasolines by contact with air to be considered.

Schulze and Buell[5] have described methods of sweetening with cupric chloride both in brine solutions and in solid state. These systems have several advantages. Since no caustic solutions are used, natural gum inhibitors are retained. With no emulsions, gasoline losses are at a minimum. With proper attention, carryover of copper mercaptides can be prevented and the treating chemical retained indefinitely. The writer's private investigation of treating with cupric chloride some time past indicated, in agreement with Schulze and Buell, that these methods often have advantages over plumbite sweetening.

Still other methods are in existence, such as the Brucite method as described by Higgins[6] which are interesting. Not all of them can be discussed here; still, the thought is left that any and all of them bear investigation in the light of economy.

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[4]Bayway Engineering Co. New York City, N. Y.
[5]W. A. Schulze and A. E. Buel. Oil & Gas Journal. Oct. 17, 1935.
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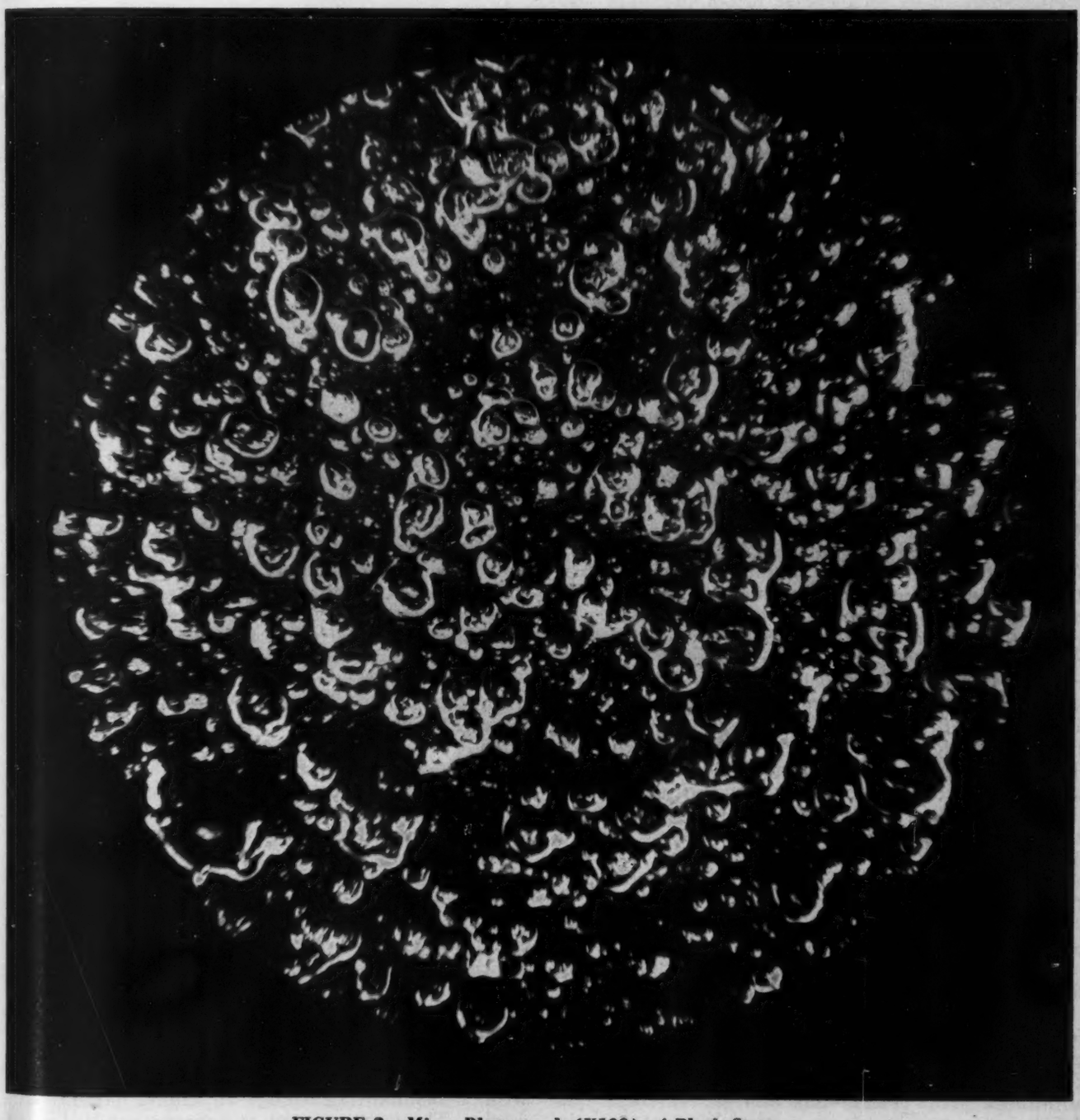

FIGURE 2—*Micro Photograph (X100) of Black Strap*

Forward Process Aromatic Fuel

WILLIAM KAPLAN
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MODERN internal combustion engines impose certain requirements on the fuels which drive them. These requirements have become more and more stringent as changes were made in engines in order to obtain higher efficiencies, the most important change being an increase in compression ratio. Of the many requirements, the most important are probably (1) the boiling characteristics, (2) the stability, and (3) the anti-knock value of the fuel.

The first and most important property for satisfactory engine operation is the boiling-point range. While it is possible to operate engines efficiently under special conditions with pure chemical compounds, it is conceded that a fuel consisting of a fairly well defined boiling-point range of hydrocarbons is required for satisfactory commercial operation. Broadly speaking, a fuel having a boiling range of about 100 to 400° F. is satisfactory in this respect for the usual varied conditions of operation to which automotive and aircraft engines are subjected.

The other two properties, stability and anti-knock, should probably be considered jointly, since it has been our common industrial experience that improved anti-knock has been obtained with some sacrifice in chemical stability. Because of the fact that our usual methods for improving anti-knock have resulted in a decrease in stability, it has been necessary to include a test such as the oxygen bomb test in our gasoline specifications.

It is probable that the first development of super fuels will always be for aviation purposes because the need of obtaining maximum power and engine efficiency is most keenly felt by this industry. At present, our goal seems to be to produce a 100.0 octane number fuel in commercial quantities. The relative importance of such a fuel is most clearly shown by Klein[1] who compared the performance of 100.0 octane fuels with a 92.0 octane aviation gasoline in two highly super-charged aeroplane engines. Tests showed that it was possible to obtain 15 percent to 30 percent more power with the 100.0 octane fuel without exceeding certain safe maximum engine cylinder head temperatures. In these tests, experimental fuels containing some tetra ethyl lead and appreciable quantities of iso-octane were used rather than fuels producible in commercial quantities.

In analyzing fuels which have been in current use, it is found that they consist of varying amounts of the four classes of hydrocarbons—paraffins, olefins, naphthenes, and aromatics.

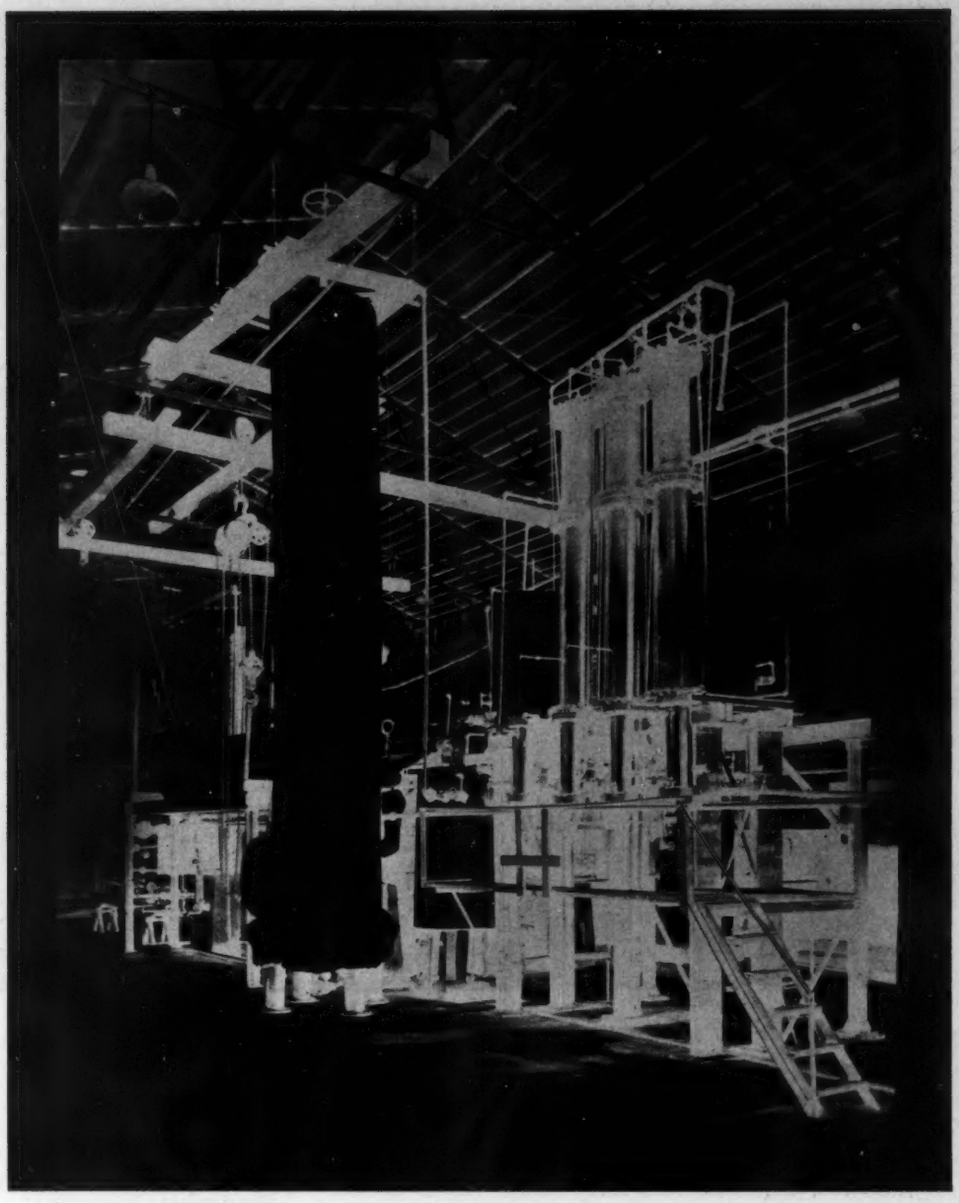
With predominantly paraffinic or straight-run fuels, the boiling characteristics can be controlled and stability has been excellent. However, if we consider iso-octane as a standard to be achieved, the anti-knock value is definitely limited. Although this deficiency in anti-knock properties does not exist in the case of the highly branched chain, paraffins having a compact arrangement of carbon atoms, there seems to be no immediate possibility of large scale production of such a fuel. Iso-octane has been produced in fair quantities, but the production of similar compounds boiling throughout the gasoline range seems rather remote. The lower-boiling paraffins possess good anti-knock properties, the higher-boiling compounds being progressively poorer and poorer in anti-knock properties. Attempts to raise the average anti-knock value have been directed to the obvious expedient of reducing the boiling range of such fuels.

The olefinic compounds possess better anti-knock properties than the straight-chain paraffins, but with a sacrifice in chemical stability. In spite of the improved anti-knock properties, these compounds do not compare with iso-octane as a standard. As with the paraffins, the more compact the arrangement of carbon atoms, the better the anti-knock value. Also, as the boiling point increases, the compounds become poorer in anti-knock properties.

The naphthenes also possess better anti-knock properties than the paraffins and are chemically stable. While better than the olefins, the naphthenes are considerably poorer than iso-octane in anti-knock value. As with the paraffins and olefins, the anti-knock value becomes progressively poorer as the boiling point of the compound increases.

Considering iso-octane as a standard of achievement, the aromatics offer an opportunity for producing a fuel which can compare favorably with it in anti-knock properties. In addition, these compounds are chemically stable. Although there is some depreciation in anti-knock as the boiling point increases, practically all of the aromatics are superior to iso-octane. This is shown in Figure I in which the anti-knock value is plotted against boiling point, using the critical compression data of Lovell, Campbell and Boyd[2]. The curves for the paraffins, olefins and naphthenes are also shown.

While it has long been recognized that a fuel composed substantially of aromatics would be highly desirable, it was generally believed that the only possible source of such a fuel in large quantities would be from the coal tar industry. In spite of its excellent anti-knock properties, motor benzol was considered unsatisfactory because it contained predominantly the single aromatic compound benzene with a resultant deficiency in higher boiling aromatics. The large amount of benzene resulted in an

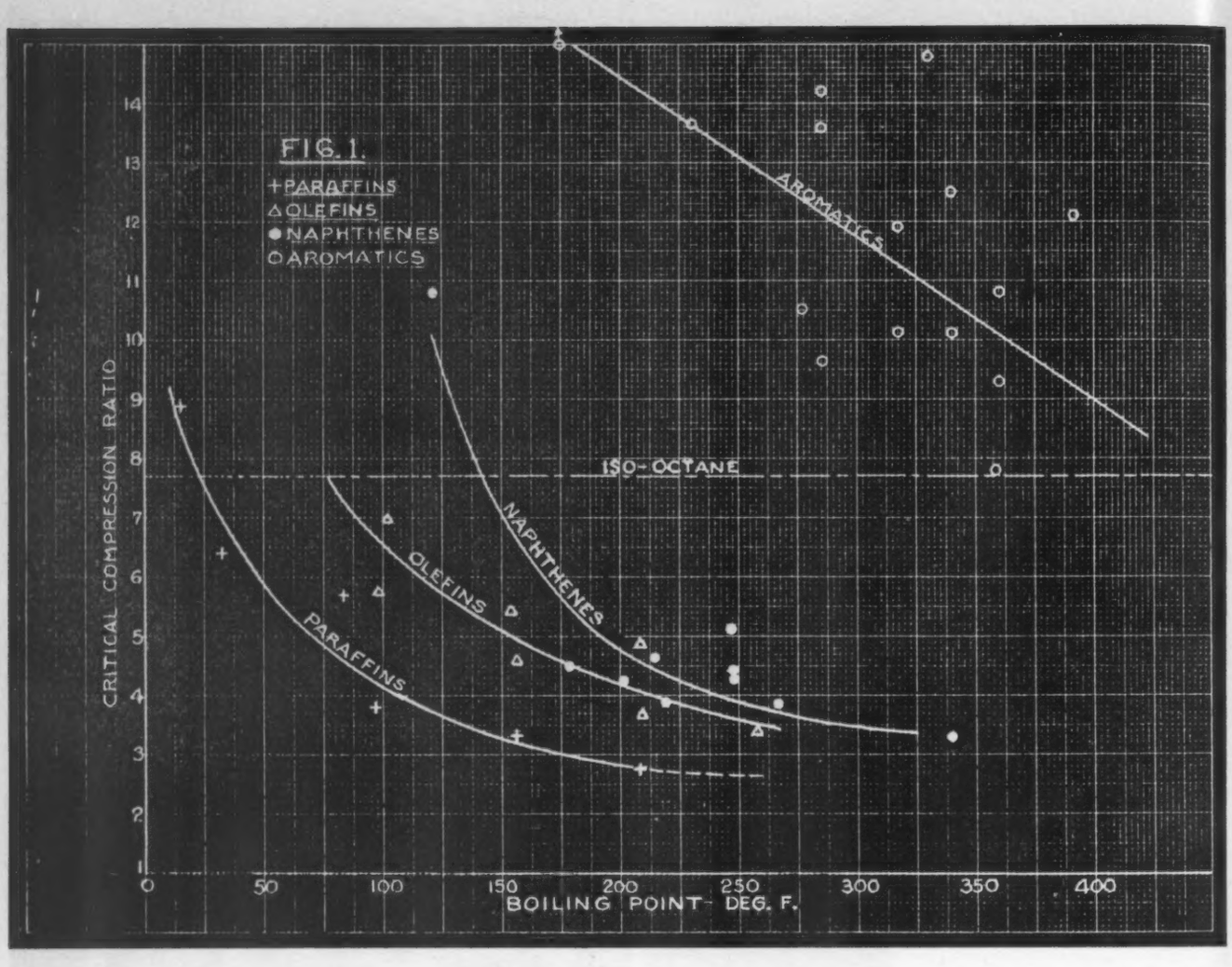


undesirably high freezing point and the narrow boiling range would not permit the smooth operation under constantly varying conditions that result from a wide boiling range fuel; hence motor benzol has been used mainly as a blending agent.

A fuel which does not possess the undesirable characteristics of motor benzol and which is composed of aromatic compounds boiling through a wide range has been produced on a semi-commercial Forward cracking unit[3]. Unlike motor benzol, which contains about 70 percent of a single aromatic benzene, this fuel contains as high as, or more than, 75 percent substituted benzenes. Because of the large proportion of substituted benzenes, this fuel has a freezing point of below minus 90° F. Although the simplest aromatic compound, benzene, boils at the relatively high temperature of 176° F., it should not be difficult to add other low-boiling compounds in order to obtain satisfactory distillation characteristics without too much sacrifice in anti-knock value.

In the manufacture of this fuel, a distillate oil was passed through a long cracking coil and carbon settling chamber where the oil was subjected to cracking and polymerization reactions. In this unit, after preheating to above 900° F., oil was passed through the 1-inch cracking coil which was over 2300 feet long. At a charging rate of 180 G.P.H. the temperature leaving the coil was about 1050° F., while the temperature in the chamber was 1050-1075° F., the pressure being 225 pounds. The cracked vapors leaving the top of the chamber were suddenly chilled by means of a water spray and passed to a condenser. Since no dephlegmator was used, the product was recovered as a synthetic crude from which the gasoline boiling fraction was subsequently distilled. With the particular unit used, the vapors were condensed at 30 pounds pressure, no attempt being made to recover gasoline boiling constituents from the noncondensable gas.

Operating with a gas oil charge, a synthetic crude was recovered having a gravity of 14.1° A.P.I. A sample of this synthetic crude was first treated for the separation of the gasoline fraction from the residue. This was done by making a continuous flash distillation of the synthetic crude, taking a benzene cut off as distillate, and then distilling the benzene



batch through a Hempel column. The following yields of products were obtained from the synthetic crude:

Gasoline (410° E. P.)	51.6 percent
Benzene Bottoms	5.8
Residuum (1.2 Sp. Gr.)	41.7
Loss	0.9

The following properties are characteristic of the type of gasoline recovered:

°A. P. I.	31.3
Sp. Gr.	0.869
I. B. P.	133° F.
10 percent	217° F.
20 percent	230° F.
50 percent	266° F.
80 percent	317° F.
90 percent	343° F.
Maximum	399° F.
Rec.	98 percent
Mol. Wt.	105
Aniline Point °C.	0.0
Refractive Index	1.4926

It will be noted that the specific gravity of this fuel is high, 31.3° A.P.I. being usually considered as within the range of high boiling gas oils. This specific gravity, however, is consistent with the highly aromatic nature of the gasoline. The aromatics are further indicated by the low aniline cloud point and the high refractive index. When subjected to hydrocarbon analysis, by the two commonly used methods, the fuel contained the following:

	Method I (a)	Method II (b)
Olefines	4.8 percent	8.6 percent
Aromatics	85.4 "	91.4 "
Naphthenes	9.8 "	0.0 "
Paraffins	0.0 "	0.0 "

(a) Olefines calculated from Bromine Number; olefines plus aromatics removed by three treats with 91 and 98 percent sulfuric acid.

(b) Olefines removed with 80 percent sulfuric acid and redistillation; aromatics by nitration.

In order to learn more of the nature of the aromatic compounds present, a portion of the benzene was carefully fractionated through a 3-foot chain-filled column to a vapor temperature of 290° F. This included the benzene, toluene and xylene fractions. The residue from this distillation was then fractionated over a 12-inch column into rather wide boiling range cuts which were then distilled one at a time into 5° F. cuts in order to separate as well as possible the various hydrocarbons from each other.

The first three hydrocarbons of the aromatic series, benzene, toluene and xylene, separated by distillation over a 3-foot column, are thought to have a fairly high state of purity. During the distillation, the thermometer remained very close to the boiling point of the hydrocarbon and then made a rather rapid rise to the next higher boiling one with very little distillate coming over in between. The presence of these compounds has been further confirmed by physical and chemical tests. The compounds boiling above the xylenes were separated somewhat roughly by making 5° F. cuts during the redistillation. From the 3-foot column distillation, a fairly accurate idea

is had of the amounts of benzene, toluene and xylene present, but because of the overlapping in boiling range and lack of a definite quantitative method, we can only indicate in a qualitative way some of the compounds present in the higher-boiling fractions of the gasoline.

The table below shows some of the aromatic hydrocarbons which were definitely identified in the indicated cuts from the Forward distillate having the same approximate boiling point. The specific gravity, refractive index and molecular weight of the cuts also is given. It must be realized that the cuts overlap one another because of the inefficiency of the fractionating column, so that compounds may be present in a fraction which actually have a higher or lower boiling point than that of the pure compound. The possible presence of azeotropic mixtures may also contribute to this same result.

Investigation of Aromatic Fuel

Boiling Range °F.	Specific Gravity	Refractive Index	Molecular Weight	Compound Present
84—168	.7651	1.432	....	
168—200	.8594	1.4828	79	Benzene
200—220	.8604	1.483	....	
220—241	.8654	1.4898	88.3	Toluene
241—274	.8618	1.4877	95	
274—290	.8674	1.4977	102	Xylene
290—315	.8724	1.4957	108	Isopropyl Benzene
315—320	.8734	1.496	113	*n*—Propyl Benzene, *o*—Methyl Ethyl Benzene, Methyl Isopropyl Benzene
320—325	.8748	1.4973	115	*p*—Methyl Ethyl Benzene
325—330	.8764	1.4982	117	Mesitylene
330—335	.8823	1.5021	119	Pseudocumene
335—340	.8853	1.5033	121	Sec. Butyl Benzene, Isobutyl Benzene
340—345	.870	1.5059	123	
345—350	.8934	1.5073	126	*o*— and *p*— Methyl Isopropyl Benzene
350—355	.8954	1.5078	128	
355—360	.8997	1.5107	130	*n*—Butyl Benzene, *o*—Methyl Propyl Benzene
360—370	.9008	1.5113	130	*o*— and *p*—Diethyl Benzene
370—380	.9038	1.5127	130	
380—390	.9258	1.5294	130.3	Iso-amyl Benzene
390—400	.9426	1.5422	130	*n*—Amyl Benzene
400—422	.9676	1.5634	132	Naphthalene
422—450	.9946	1.4892	133	

The three lower members of the series benzene, toluene and the xylene, were identified by making the di- or tri-nitro derivatives and determining their melting points. The higher members of the series of substituted benzenes were identified by the type of acid produced after the fraction had been oxidized with potassium permanganate solution. This procedure required the boiling of a mixture of the hydrocarbon with potassium permanganate solution for a period of six to eight hours on the steam bath. This formed the various types of acids shown below, depending on the number and position of the alkyl radicals on the benzene ring. For example, a mono substituted benzene was oxidized to benzoic acid.

(1) $C_6H_5C_2H_5 + O \rightarrow C_6H_5COOH + H_2O + CO_2$

which was identified by the formation of aniline blue by the action of aniline, fuchsin and benzoic acid. The alkyl group in this case being oxidized to carbon dioxide, water and a $-\overset{O}{\overset{\|}{C}}-OH$ or carboxylic acid group.

In the case of a di-substituted benzene, we have three possibilities depending on the relative position of the two groups to each other. With the groups in the ortho position, phthalic acid is formed thus

(2) $C_6H_4(CH_3)(C_2H_5) + O \rightarrow C_6H_4(COOH)_2 + CO_2 + H_2O$

Phthalic Acid

In the case of meta positioned groups, isophthalic acid is formed

(3) $C_6H_4(CH_3)(C_2H_5) + O \rightarrow C_6H_4(COOH)_2 + CO_2 + H_2O$

Isophthalic Acid

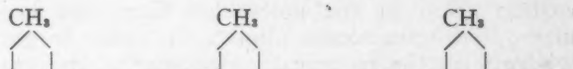
In the case of para positioned groups, terephthalic acid is formed:

(4) $C_6H_4(CH_3)(C_2H_5) + O \rightarrow C_6H_4(COOH)_2 + CO_2 + H_2O$

Terephthalic Acid

The above acids were identified by the following tests: When phthalic acid is heated with a crystal resorcinol and a drop of concentrated sulfuric acid at 160° C. for 3 minutes, a fluorescein is formed which may be identified by the characteristic yellowish-green fluorescence of its sodium compound in water. Isophthalic and terephthalic acids were identified by means of the melting point of their dimethyl esters made by the treatment of the acid with phosphorus pentachloride and methyl alcohol.

The tri substituted products were identified in the case of mesitylene and pseudo cumene by the melting point of the trinitro derivatives. Other tri substituted compounds within the gasoline range oxidize to:



Xylic Acid m. p. 126° C. — Mesitilinic Acid m. p. 166° C. — Uvitic Acid m.p. 287°C.

None of these other tri substituted compounds were identified however because of the presence of other acids in the products of oxidation which prevented the taking of accurate melting point data. No chemical method of identification was available so that the presence of this type of hydrocarbons could not be proved definitely. The presence of naphthalene was proved by means of the melting point of the hydrocarbon which had been purified by recrystallization.

The presence of naphthalene begins to show itself in the cuts boiling around 375° F. as indicated by the increase in the specific gravity and refractive index and also the drop in molecular weight after a steady increase. This shows the compounds to be getting poorer in hydrogen and to have the double benzene ring structure. The experimentally determined molecular weights correspond very well with those for the compounds found in the various cuts until the presence of double ring compounds cause a sudden drop in the experimental values found, which caused quite a wide divergence in the values obtained and those shown by the various substituted benzenes.

It is to be regretted that no quantitative figures can be obtained as to the amounts of the various aromatic hydrocarbons present. However enough evidence has been obtained to show that there is a great number of aromatic compounds present to a degree even greater than from coal tar distillation.

REFERENCES:

[1]Journal of the Institute of Aeronautical Sciences, Vol. II, No. 2.
[2]Ind. Eng. Chem., Vol. 26, No. 10, page 1105-1107.
[3]Covered by U. S. Patent No. 2,007,081.

Natural Gas As a Chemical Raw Material

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THE hydrocarbons of natural gas are classified as paraffins, the designation signifying that such compounds have small affinity. In other words the paraffin hydrocarbons were once regarded as chemically inactive because of their apparent stability with most reagents. However, it is now believed to be generally recognized among chemists that the designation of these compounds as paraffins was a misnomer; there being many reagents with which these substances will react once the proper conditions are provided. The difficult part has been to control the reactions after their initiation. All of the paraffins starting with methane have the general formula $C_nH_{2n}+_2$ which signifies that for every carbon atom in the molecules there are twice as many hydrogen atoms plus 2. In order to get anywhere with the chemical processing of the paraffins it is first necessary to eliminate part of the hydrogen or replace it with something else.

METHANE

Methane is the simplest hydrocarbon and the most abundant. It is also the most difficult to react. The formula is CH_4 and it has a molecular weight of 16.03.

Methane will react with chlorine to produce methyl chloride, dichloromethane, chloroform and carbon tetrachloride corresponding respectively to the formulas

CH_3CL, CH_2Cl $CHCl_3$, and CCl_4.

Hydrochloric acid gas HCl, is a by-product of these reactions. The reacting weights based on 1 pound of methane are as follows:

(1) 1 lb. methane + 4.43 lb. chlorine = 3.15 lb. methyl chloride + 2.28 lb. hydrochloric acid gas.
(2) 1 lb. methane + 8.86 lb. chorine = 5.40 lb. dichloromethane + 4.56 lb. hydrochloric acid gas.
(3) 1 lb. methane + 13.29 lb. chlorine = 7.45 lb. chloroform + 6.84 lb. hydrochloric acid gas.
(4) 1 lb. methane + 18.72 lb. chlorine = 10.60 lb. carbon tetrachloride + 9.12 lb. hydrochloric acid gas.

OPERATING MARGIN (THEORETICAL)

Methane	= $0.002 lb. at $0.084 per 1000 cu. ft.
Chlorine	= $0.002 lb. at $0.084 per 100 cu. ft.
Hydrochloric Acid	= $0.05 in carboys 36 percent.
Methyl Chloride	= $0.45 in drums.
Dichloromethane	= $0.25 assumed.
Chloroform	= $0.20 in drums (technical).
Carbon Tetrachloride	= $0.0525 in drums.

(1) $(1 \times 0.002) + (4.43 \times .02) = \$0.0906$
$(3.15 \times 0.45) + (2.28 \times .05) = \$1.5310$
Difference = 1.4404

(2) $(1 \times 0.002) + (8.86 \times 0.02) = \$0.1792$
$(5.40 \times 0.25) + (4.56 \times 0.02) = \$1.4412$
Difference = 1.2620

(3) $(1 \times 0.002) + (13.29 \times 0.02) = \$0.2678$
$(7.45 \times 0.20) + (6.84 \times 0.05) = \$1.8320$
Difference = 1.5642

(4) $(1 \times 0.002) + (18.72 \times 0.02) = \$0.3764$
$(10.60 \times 0.0525) + (9.12 \times 0.05) = \$1.0145$
Difference = 0.6381

The above calculations are based upon 100 percent yields only for purposes of comparison. The theoretical margin of profit, however, is shown to be such as to provide considerable allowance for development and processing costs even for processes of low efficiency. In all cases the cost of the methane is negligible in comparison with the cost of chlorine. The present low price of chlorine should add incentive to further development of manufacturing processes.

The reactions between chlorine and methane give off much heat, that is, they are strongly exothermic. There are many ways to induce these reactions. The main difficulty has been to control the reactions so as to avoid explosion and produce the desired chloro-derivatives. The reaction under (1) for the production of methyl chloride evolves about 3700 B.t.u. per pound of methane chlorinated. In order that such reactions be controlled it is necessary that much of this heat be rapidly dissipated.

Jones, Allison and Meighan, U. S. Bureau of Mines Technical Paper 225, 1921, noted that when the temperature of reactions rose above 500° C. (932° F.) only hydrochloric acid gas and free carbon resulted in accord with the reaction.

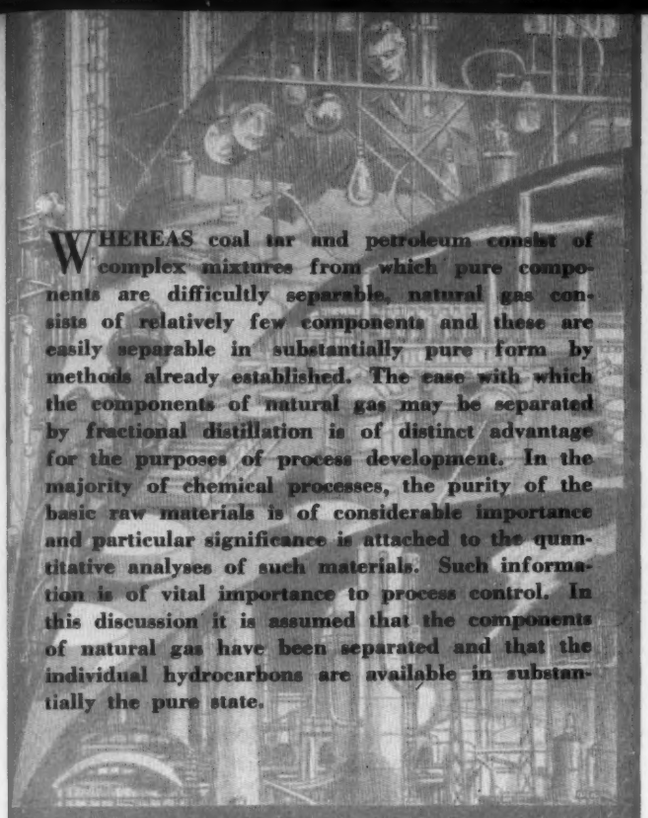
$$CH_4 + 2Cl_2 = C + {}_4HCl$$

A patent for producing carbon black in accord with the above reaction was taken out by Mott, U. S. Patent 1,259,121, March 12, 1918.

Chlorination reactions may be introduced in a variety of ways, among which are exposure to heat, light catalysts, chemical reagents and electric discharge.

For the thermal chlorination of methane various expedients have been used. Colin, U. S. Patent 427,944, May 13, 1890, advocates a reaction chamber temperature of 212° F. to 392° F. for the chloroform reaction. The hydrochloric acid gas was removed from the reaction mixture by water washing.

Weickel (J. S. C. I., 1915, 341116) prepared methyl



WHEREAS coal tar and petroleum consist of complex mixtures from which pure components are difficultly separable, natural gas consists of relatively few components and these are easily separable in substantially pure form by methods already established. The ease with which the components of natural gas may be separated by fractional distillation is of distinct advantage for the purposes of process development. In the majority of chemical processes, the purity of the basic raw materials is of considerable importance and particular significance is attached to the quantitative analyses of such materials. Such information is of vital importance to process control. In this discussion it is assumed that the components of natural gas have been separated and that the individual hydrocarbons are available in substantially the pure state.

ENGINEERING ECONOMICS

chloride by using 10 volumes of methane to 1 volume of chlorine at or below 752° F. and a contact period of approximately 10 seconds. The methyl chloride produced along with other chloro-derivatives was separated by fractionation from the water washed reaction mixture. There are numerous other processes of thermal chlorination described in the literature, all of which expend more or less upon the use of large volume ratios of methane to chlorine. In all these reactions, time, temperature, and proportions of mixture are the main variables. Intimate mixing and rapid heat dissipation from the reaction mixture are obviously of paramount importance.

For the catalytic chlorination of methane, charcoal seems to be the favored catalyst. Temperatures as low as 86° F. to 194° F. are mentioned for reaction using animal charcoal. Mixed chlorides usually result from all these reactions using catalysts. Among the catalysts mentioned in the literature are animal charcoal, coke, activated carbon, iron, copper, antimony, chlorinated paraffin oils, molten ferric and cupric chlorides. The gist of the use of all these catalysts seems to be due to individualistic tendencies on the part of the investigators.

When methane and chlorine are exposed to sunlight, the mixtures react with explosive violence. This observation has probably been verified by most freshmen chemists. This photo chemical phenomenon has instigated much conjecture and has been the basis of many investigations dealing with light effects. Ultra violet radiation, mercury vapor light, actinic rays, blue light and light of varying intensities have all been used with more or less satisfactory results. Wave lengths of about 2530 Angatrom units are stated to be especially suitable. The silent electric discharge has also been used with considerable success.

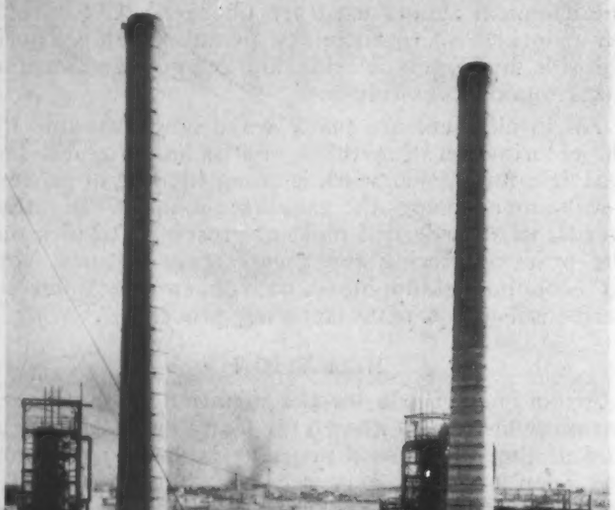
Because of the violence of reactions between gaseous methane and chlorine wherein the large amount of heat rapidly generated has made control difficult, chlorinating agents have been resorted to. Among the chemical agents used are phosgene, $COCl_2$, sulfur chloride, S_2Cl_2, antimony pental-chloride, cupric chloride, hydrogen chloride, and oxygen, and various other metallic chlorides.

All in all there are many ways now available for the chlorination of methane and its homologues. The real field for further work is along the line of process development using the small-scale plant. In other words, what is needed most at present is to pick out the process offering the greatest possibilities from an economic standpoint and concentrate upon its perfection into a manufacturing process.

NITRATION

Although methods for the nitration of the higher paraffins have been known for many years, the nitration of the lower paraffins, that is, below pentanes. has been reported only recently. See J. I. E. C., March, 1936, page 339, "Nitration of Gaseous Paraffins" by Hoss, Hodge and Vanderbilt. These authors state as follows: "Nitro paraffins were first produced in 1872 by Meyer who prepared them by the reaction which bears his name, i. e., metathesis of an alkyl halide with silver nitrite. Although Beilstein and Kurbatow obtained mono-nitrocyclohexane in 1880 by the nitration of a petroleum fraction, the nitration of the paraffin hydrocarbons was first studied in the years between 1892 and 1907. * * * In spite of this discouraging situation, the study of the nitration of the gaseous paraffins was begun in this laboratory in 1930 because of the following considerations: (1) The abundance and low cost of the simpler paraffin hydrocarbons which are available in a condition of high purity; (2) the paucity of the modes of chemical attack to which these hydrocarbons are susceptible; (3) the absence from the literature of any recorded nitration of saturated hydrocarbons of less than 5 carbon atoms; (4) the fact that nitric acid can be produced by the oxidation of synthetic ammonia at a cost of approximately $0.0175 per pound (anhydrous basis) and (5) indications in the literature that these compounds would be of value if they could be produced at low cost." Briefly, the method of operation described by these authors was to pass the hydrocarbon vapor through nitric acid heated to 108° C., which gave a hydrocarbon-nitric acid vapor ratio of about 2 to 1. The product obtained separated into two layers, the upper consisting of nitro-paraffins and the lower of dilute nitric acid. Tertiary nitro-butane (22 percent yield) was obtained from isobutane and was nitrated in sealed tubes. Favorable results were reported for the nitration of ethane, propane, butane and isobutane. Negative results were obtained with methane. Acetone nitro-methane, nitro-ethane, two nitropropanes, and 3 nitro-butanes were identified among the products of reaction.

These authors state that (1) yields are practically constant between 150° C. to 420° C., but the ratio of components varied with temperature; (2) mixing nitric acid with free oxygen favors the oxidation reaction with no increase in nitration; (3) oxides of nitrogen are excellent oxygen carriers; (4) increasing pressure increases yield and greatly increases the reaction rate; (5) the yield of nitro paraffins increase with hydrocarbon gas to concentration up



Thermal Process Polymerization Units, Phillips Petroleum Company, Borger, Texas.

to a ratio of 14 to 1, and (6) no catalyst was found which increased the yield of nitro paraffins.

SULPHONATION

There are indications that the lower paraffins hydrocarbons may be sulphonated by the use of concentrated or fuming sulfuric acid. Worstall (Amer. Chem. Jr., 1898, 20, 664) noted the formation of sulphonic acids from the reaction between fuming sulfuric acid with normal hexane, normal heptane and normal octane. The action of sulfur trioxide on the higher paraffins above C_5 has been noted by a number of investigators. The absorption of methane, ethane, propane, isobutane and butane has also been observed. Most of these reactions have been of a complicated character and the products of reaction have been complex mixtures not susceptible to easy identification.

The author has noted a violent reaction to take place with natural gas hydrocarbons and chlorosulphonic acid. The sulphonic acids have the formula

$$C_nH_{2n+1}\ SO_2.\ OH$$

The sulphonic acids may be fused to the corresponding alcohol by heating with solid alkalies such as caustic soda or calcium hydroxide. A typical reaction for the production of ethyl alcohol would be

$$CH_3SO_3Na + NaOH = C_2H_5OH + Na_2SO_3$$

The possibilities for the manufacture of alcohols from the hydrocarbons of natural gas seems to have been not thoroughly investigated.

OXIDATION

The saturated hydrocarbons of natural gas react with oxygen in varying degree, depending largely upon the methods used for conducting the reaction. The oxidation reactions are similar to chlorination in many ways, i. e., there is a great amount of heat evolved and the period of reaction is very short. The main difficulty involves control rather than initiation of reaction. The wide spread between the cost of raw materials and the value of the oxidized product makes processes of this nature of economic importance. Air is free and natural gas is very cheap in many localities.

There are two main theories of oxidation as applied to the saturated hydrocarbons, namely the hydroxylation theory advanced by Bone and his collaborators and the peroxide theory advanced by later investigators. There is considerable evidence to support both theories, and the complete story will probably consist of a combination of the two theories. Molecular oxygen may in part disrupt into atomic oxygen prior to reaction with the hydrocarbon and thus produce either alcohol or aldehyde depending upon pressure, temperature, proportions of reactants, and the period of reaction. The glow or induction period which has been noted by some investigators may be due to the transformation of molecular oxygen to atomic oxygen due to intimate contact with the surfaces of hydrocarbon molecules.

The equations for the hydroxylation of methane would be

$$CH_4 + O_2 = CH_4 + O + O$$
$$2\ CH_4 + O + O = 2\ CH_3\ OH$$

by reaction with molecular oxygen

$$CH_4 + O_2 = CH_2\ (OH)_2 = H.CHO + H_2O$$

The formation of the peroxide would be

$$H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-H + O_2 = H-\overset{\displaystyle H\text{-}O}{\underset{\displaystyle O\text{-}H}{C}}-H = H.CHO + H_2O$$

Inasmuch as there is extensive demand for cheap wood alcohol (CH_3OH) as well as for formaldehyde (H_1CHO) the solution of these theories is of industrial importance.

Newitt and Haffner (Brit. Chem. Abs. A, 1932 232), using a reaction mixture consisting of 9 parts methane and 1 part oxygen under a pressure of 1500 pounds per square inch at 360° C. for a period of several minutes, found that the oxygen had disappeared and that the reaction was complete. The reaction products consisted of 17 percent methyl alcohol, 0.6 percent formaldehyde, carbon monoxide, carbon dioxide and water.

The higher homologues of methane have been oxidized to unsaturates, alcohols, aldehydes, ketones, acids and polymerization products. Pure oxygen ozone, oxides of nitrogen, metallic oxides as well as air have been used as oxidizing agents. The oxides of nitrogen when mixed with air are very efficient oxygen carriers.

THERMAL DECOMPOSITION

When heated sufficiently the saturated hydrocarbons decompose into hydrogen and carbon. However, when heated to a lesser degree decomposition may be accompanied by synthesis resulting in the production of complex hydrocarbon mixtures. Methane is by far the most stable of the hydrocarbons toward heat. Its decomposition by heat was first noted in 1808 by Dalton and Henry, using an electric spark, electrically heated platinum wire, or passing through a red hot tube. For the production of polymerized products from methane a short reaction period and high temperature appears to give the best results. Temperatures between 1000° C. and 1200° C. and periods of 1/3 second have been used by Fischer, Wheeler, and Wood and Stanley and Nash, using porcelain or quartz tubes. Acetylene, unsaturated hydrocarbons, benzene, toluene, xylene and naphthaline were among the products reported as resulting from this treatment. There appears to be considerable diversion of opinion among investigators as to mechanism of methane pyrolysis. Some hold that ethylene is a primary product of molecular disintegration whereas others maintain acetylene is first formed. Due to the difficulty of determining the mechanism at the time of reaction, investigators have necessarily relied up analyses of the reaction products. Kassel (J.A.C.S. 1932, 54, 3949) by thermodynamic interpretation of the results obtained in his experiments assumed the following reactions to take place:

$$CH_4 \rightleftharpoons CH_2 + H_2$$
$$CH_2 + CH_4 \rightleftharpoons C_2H_6$$
$$C_2H_6 \rightleftharpoons C_2H_4 + H_2$$
$$C_2H_4 \rightleftharpoons C_2H_2 + H_2$$
$$C_2H_2 \rightleftharpoons 2C + H_2$$

Subsequent investigators have found evidence supporting the theories of Kassel. In the pyrolysis of methane the object is to obtain the maximum yields of liquid products. In order to do this, it is necessary to eliminate part of the hydrogen from the CH_4 molecule and then polymerize the residual carbon-hydrogen fragments. As the hydrogen-carbon ratio is higher for methane than for the successive homologues such as ethane propane, butane and isobutane, a greater amount of attention has been directed toward pyrolysis of these higher hydrocarbons. However, methane is by far the more abundant of the natural gas hydrocarbons and therefore its transformation into more valued products is of exceptional industrial significance. For example, if 1000 cubic feet of methane which under standard conditions weighs approximately 42 pounds would be converted into benzene in accordance with the equation

$$6\ CH_4 = C_6H_6 + 9H_2$$

the yield of benzene would be approximately 34 pounds = 4.7 gallons. Naturally theoretical yields are not to be anticipated, but even a 25 percent yield would be of interest.

STEAM REACTIONS

At high temperatures using catalysts, steam reacts with the saturated hydrocarbons producing carbon monoxide, carbon dioxide and hydrogen in accordance with the general equation

$$C_nH_{2n} + 2 + N_2 + H_2 = NCO + NCO_2 + (N+1)H_2$$

The chief industrial value of this reaction has been for the production of hydrogen. However, part of the products of this reaction may be reacted to produce alcohol in accordance with the equation

$$CO + 2H_2 = CH_3\,OH.$$

Among the catalysts mentioned for hydrogen production are nickel-magnesium oxide, nickel, cobalt, chromium, nitrates of cobalt, nickel and aluminum, reduced nickel oxide, activated vegetable carbon and nickel using metallic oxides such as alumina, iron, etc., as promoters. These reactions have been more thoroughly investigated than others mentioned heretofore in this discussion.

CARBON MONOXIDE AND CARBON DIOXIDE

One rather interesting possibility is the theoretical reaction between carbon dioxide and methane for the production of acetic acid.

$$CH_4 + CO_2 = CH_3COOH$$

Patents for the production of acetic acid using mixtures of carbon monoxide, carbon dioxide and methane have been taken out by Dreyfus and Boder, U. S. Patents 1,864,551 and 1,864,643. The reaction temperatures vary between 120° C. and 350° C. under pressures of 12 atmospheres to 500 atmospheres using various catalysts such as, for example, nickel carbonate.

The main reactions between carbon dioxide and methane seem to be

$$CH_4 + CO_2 = 2\ C + 2H_2O$$

This reaction has possibilities from the standpoint of the manufacture of carbon black. The reaction

$$CO_2 + CH_4 = 2\ CO + 2\ H_2$$

also takes place. The foregoing reaction is favored by low pressures (below atmospheric).

MISCELLANEOUS REACTIONS

Reactions have been obtained between hydrogen, nitrogen and methane at very high temperatures. The results are only of academic interest. Hychoyanic acid gas was obtained among the products of reaction. Ammonia also reacts with methane at high temperatures as represented by the equation

$$CH_4 + NH_3 = HCN + 3\ H_2$$

No reactions between sulfur and the lower paraffins have been reported so far as is known to the writer. Sulfur, however, is known to react with paraffin wax producing hydrogen sulfide and dark complex residues. One of the more interesting possibilities aside from the straight chemical reactions is the use of the silent electric discharge. The usual effect is said to be dehydrogenation with subsequent polymerization. Lind and Glochler (J.A.C.S., 1928) using ethane found that the nature of the liquid product could be regulated if the liquid products formed were immediately removed from the walls of the reactor. These investigators obtained liquids varying in molecular weights between 105 and 467. Low pressures and temperature appear to favor the for-

mation of liquid products. The action of the silent electric discharge is stated to be similar to that of alpha-radiation. Voltages of 12,000 to 20,000 were used.

DISCUSSION

From the foregoing brief review it is apparent that natural gas is far from being a chemically inactive material. The higher hydrocarbons such as ethane, propane, butanes, etc., are more active than methane. The chlorides of methane, ethane, propane, etc., may be considered as basic raw materials for the manufacture of other organic chemicals. One industrial process consists of reacting methylchloride with milk of lime at 167 pounds square inch to 260 pounds square inch at a temperature of 190° C. The equation is

$$2CH_3Cl + Ca(OH)_2 = 2\ CH_3OH + CaCl_2$$

Lacy, U. S. Patent 1,253,055.

In another industrial process methyl chloride and steam are passed through a series of reaction chambers containing hydrated lime which is continuously charged counter-current to the passage of the vapors. The pressures mentioned are 175 to 200 pounds per square inch at temperature of 350° C. to 450° C. This is MacMullen and Gegenheimer U. S. Patents 1,549,779 and 1,641,544, assigned to Mathieson Alkali Works, Inc. The higher alcohols may be made in a similar way by using the higher alkyl nonchlorides. A side reaction produces the ethers $CH_3\ OCH_3$, $C_2H_5\ OC_2H_5$, etc. The hydrolysis of the higher alkyl halides is more difficult than for methyl chloride because of their tendency to decompose into unsaturates and hydrochloric acid. All of the alkyl chlorides offer interesting possibilities from the standpoint of process development. Amyl alcohols, amyl acetates, and amyl ethers are now manufactured on an industrial scale by the hydrolysis of mono-chlorpentane

$$C_5H_{12} + Cl_2 = C_5H_{11}\ Cl + HCl.$$

In fact, the possibilities for the use of natural gas as a chemical raw material cannot be over-emphasized.

Sinclair Plant No. 12, Seminole, Oklahoma.

Oiliness

Its Meaning and Value In Motor Oils Practice and Theory*

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PART I

WHEN, 12 years ago, the author started his research work on lubrication and oil, it happened that the problem "that one lubricant may give a lower coefficient of friction than another of the same viscosity" was the first he had to face.

The "definition" of this "property" and the technical research work on the subject, the results of which made an excessive use, for explanation, of molecular forces acting over great distances, did not appeal from a physico-chemical point of view.

Obviously there were too many factors involved in this "property." Thus, it seemed desirable first, to push the hydrodynamic theory of lubrication as far as possible on a physico-chemical basis. The author advanced, in 1928, the hypothesis of molecular flow-orientation and consequent drop of viscosity under bearing operating conditions and demonstrated by means of machines designed by Prof. Prandtl, that motor oils (about SAE 50) are easily oriented at normal operating speeds, yielding a drop in viscosity of 10-17 percent. The experiments further demonstrated that down to film thicknesses of 0.0023 mm (0.00009 in.) the laws of hydrodynamics hold[1]. It follows from theoretical reasons that, the longer the molecules, the easier they must orient themselves in the direction of flow and it is obvious that spherical molecules cannot show this sort of orientation, i.e., the lower the journal speeds at which orientation starts, the longer the molecules must be. It will be shown later that the machine measures two factors; not only the drop in viscosity by flow-orientation but also (in a qualitative way) one factor of "oiliness"—the comparative length of the molecules.

It is beyond the scope of the present paper to give a historic survey of the oiliness question, for it would be more misleading than useful. However, a careful consideration of the properties an oil should have to undergo minimum deterioration in and to prevent with maximum efficiency, wear of the motor will reveal useful information. Such consideration must be based both upon practical experience with actual motor performance and upon a lot of physico-chemical reasoning which is bound to look horribly academic until the surprising fact emerges, that in the end we are none the wiser as to any "definition" of "oiliness." However, we get a pretty definite answer as to the properties an oil should have. Incidentally we shall see just where the possibilities and limits of improvement are and that our rather vague "oiliness" is split up into a number of very definite physical notions which are, at least in principle, tangible and for most of which methods of measurement are available. The author does not claim to have made anything like a great discovery and begs to state that the laws of nature look so simple, the very moment one gets them separated.

CAUSES OF MOTOR WEAR

First start with the question: Which are the causes of motor wear?

I. Basing upon his own practical and scientific research work in this field and upon a few other well established facts, the author wishes to emphasize that a well designed motor with mirror finish surfaces, under ideal operating conditions, reasonable oil viscosity, normal operating temperatures and no dust, should show no wear and there should be no need of "oiliness," whatever that word may mean.

II. The causes of wear under actual normal operating conditions are:

(1) Mineral dust, (2) poor initial polish, (3) corrosion at low operating temperatures, (4) destruction of polish and (5) deterioration of oil. Oil carbon in itself is no grinding agent—no matter whether it is hard or fluffy. If it is free from mineral dust, its hardness scarcely exceeds the hardness of graphite[2].

We know that we cannot absolutely exclude mineral dust from entering the motor without impairing volumetric efficiency. But we can quite materially reduce the abrasive properties of fine mineral dust by a suitable oil. To understand this fully, we must gain some insight into the polishing process and how it works with different oils. The author found that oils of a low coefficient of static friction produce a better polish. The oil molecules must have the following properties: they must form films with strong lateral intermolecular cohesion. The oil molecules orient themselves on surfaces at a steep angle[3]; the longer they are, within a chemical series, the lower

*General remark: Many references, not explicitly cited in this paper, will be found in the author's article "Die physikal.—chem. Grundlagen d. Schmierungsvorgange" in the booklet "Schmierung" edited by the Deutsch-Amerikan. Petrol. Ges. Hamburg (STANDARD), quoted as "Sch." in this paper.

is their coefficient of friction and the stronger the lateral cohesion, which is proportionate to their area of intermolecular contact. I.e. this area should be interrupted as little as possible by smaller molecules. We know furthermore that viscosity—roughly—increases in one series of hydrocarbons with their length, approximately with their molecular weight[4]. Thus, to avoid excessive viscosity of the oil in bulk for hydrodynamic reasons we may resort to additions of "polar" oils to mineral oils of lower viscosity. Some of them have even a lower coefficient of friction than the highly viscous mineral oils and all of them present the advantage of a firmer anchoring to the surface with their polar group.

Comparative tests were made with two cars over 20,000 miles. Car A was run on straight mineral oil, car B on a mineral oil with a polar addition. Each piston had two ordinary piston rings and one scraper ring. With car A both the top ring and the scraper ring showed a good average polish, although the scraper ring was obviously brighter. The ring located between these showed a mirror-like polish. The rings of car B showed all a practically uniform mirror polish, the finest the author ever saw with piston rings.

Preliminary tests with a special device for polish experiments on different oils showed that the worn off metal took much longer time to sediment in the experiment on oil with the polar addition than on the same oil without the addition, although the latter was a little more viscous. These experiments and the microscopic inspection of the piston rings demonstrate that the surfaces differ just as they would differ on polishing them with various grades of emery. It is through the medium of the worn off metal, or the dust entering the combustion chamber that continuous wear is brought about. And it is the difference of the protecting and dust-enveloping film which determines rate and degree of wear. It is this process of friction and only this, into which boundary friction conditions enter and where this friction and "toughness' of film play an important part and it is obvious that low film friction plus strong lateral cohesion plus firm adhesion to the surface must be favorable. The stronger the molecular "anchoring" to the surface, the more positively is the weakest part of the protective film conferred to the "natural cleavage plane" between the protective oil layers. This "fuse"-action is perfectly definite, whatsoever the mechanism of abrasion may be. Now, the molecular forces tying a "polar" group[5] to a surface may be up to 25 times the forces of the C-H-group, hence the greater protective efficiency or safety of a polar film, all other factors being equal. It is obvious that a metal or mineral particle, covered with such a film, has less chance of cutting deep into the metal surface and breaking off big particles which in turn would repeat this process, resulting in a rough, quick wearing surface. Thus, with such a polar protective film, which wears off small particles, the surface must be polished both more quickly and more smoothly and moreover the polishing process must come to a stand-still at smaller clearances than with a film where the difference between adhesive and "cleavage" forces is small and sometimes big particles are worn off, the size of which will ultimately determine the clearance between the running parts. We see at a glance that the ultimate effect must depend to a high degree on operating conditions in a general way but particularly when straight mineral oil is used.

The experiment with car "B" demonstrates two other facts in excellent harmony with the physical properties of the substances involved. (1) Wear by dust and metal particles is minimized by the use of an "oil" the adhesion of which is stronger for the metal and dust than the adhesion of water formed during the warming up period of the motor. It is easily seen from the dipole moments[6] of water and the usual polar additions that those of the latter are greater than the moment of water, the corresponding moment of the C-H-group being about 15 times smaller than that of water. (2) Exactly the same holds true of the anti-corrosive properties of such a polar film. In simpler terms: wear, dust and the metallic surfaces are better "wetted" by the addition than by the corrosive agents. This does not hold for straight mineral oils and thus marks the limits of their efficiency.

The case of car A needs but very little explanation: dust, removal of oil by water and corrosion are the principal causes of wear of the top piston ring, dirt and grit from the crankcase of wear of the scraper ring. Both rings grind the particles in passing to a harmless size, resulting in a fine polish of the intermediate ring.

Summarizing, we see that (1) boundary friction, (2) cohesion and (3) adsorption and adhesion enter into the practical problem of wear. Starting from the pressing practical problem of wear, we got useful and applicable information on the "oiliness" problem in terms of molecular forces which lend themselves to well outlined experimental and theoretical investigation.

Now, consider one last factor: the deterioration of oil. Car B experiment gives us at least a hint, which, connected with a few well known facts. leads us toward the well known field of running properties of metals. It was shown that all solids entering the motor and motor oil are rapidly covered by a strongly adhering adsorption film of the polar addition. We see at once that any of the partly known partly suspected catalytic actions of the metal on the decomposition of the oil must be greatly hampered by the protective polar film. Furthermore, it is a well known fact that the products of oil oxidation are stronger polar than the original oil. This means that the molecular forces acting between these products and the polar addition are stronger than those between the former and the oil, another factor in favor of a protective action of the addition as far as oil deterioration is concerned.

It will be a matter of further research and of cooperation between the chemist and the physicochemist to find the additions best suited for various conditions and oils. It must be added, however, that the simplicity in principle of the problems involved should not deceive us as to the fact that there is still much research work to be done in some fields of physico-chemistry which are apparently so remote from and actually so important for the development of the oil industries.

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[3]See [1]b.

[4]Zeitschr. f. Physikal. Chem. (A) 144. p. 29. 1929

[5]"Sch." p. 38 f. and 48.

[6]"Sch." p. 40. See also Part II. and H. A. Stuart, Molekulstruktur, Berlin 1934. P. 127-152. and Kyropoulos, Verhandl. d. Deutsch. Physikal. Ges. (3) 16. (1935).

The Construction and Operation of

Natural Gasoline Plants

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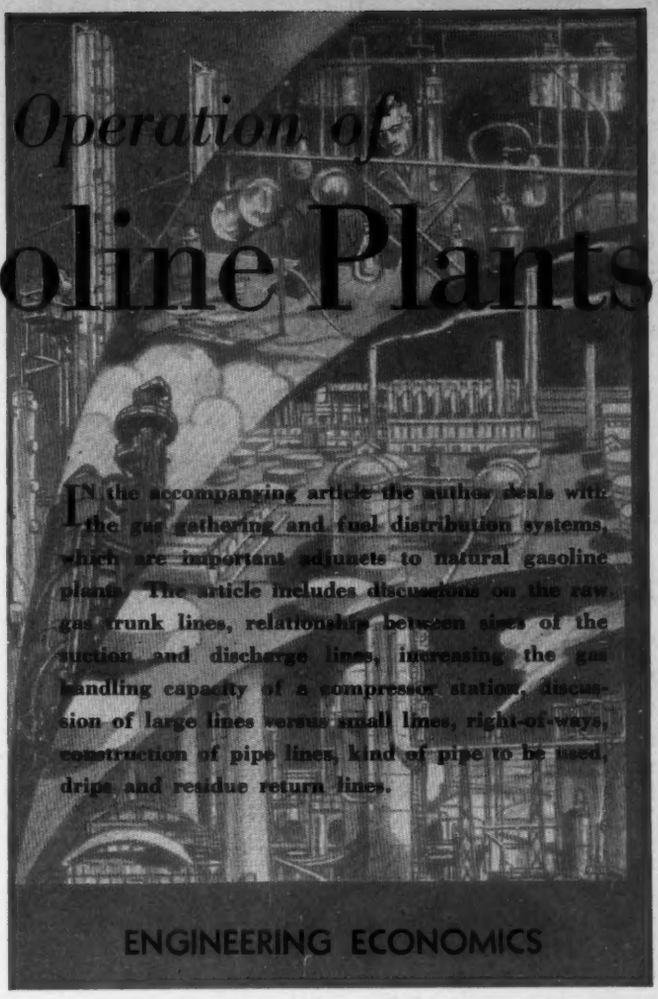
PART III


IN the accompanying article the author deals with the gas gathering and fuel distribution systems, which are important adjuncts to natural gasoline plants. The article includes discussions on the raw gas trunk lines, relationship between sizes of the suction and discharge lines, increasing the gas handling capacity of a compressor station, discussion of large lines versus small lines, right-of-ways, construction of pipe lines, kind of pipe to be used, drips and residue return lines.
ENGINEERING ECONOMICS

AS soon as the location has been made for the absorption and distillation units and the compressor stations, the work of bringing the gas from the various leases to these units and stations should be carried on with the rest of the construction program. If the field is only partially developed, the gas gathering lines must necessarily be larger than those required for handling the volumes available at the time construction is started in order to take care of future development. The decision therefore as to the size of the trunk lines must be based on:

1. The estimated amount of gas to be handled.
2. The distance the gas is to be transported.
3. The differential between the field pressure and the intake pressure at the plant.

This pressure differential of course is apt to change during the life of the field. In other words, it may be better to put in a line slightly larger than the one required to handle the large initial gas volumes at high pressure because of the decreased capacity of the line when it is forced to handle gas under reduced pressures. The decision on this point should be based largely on previous experience in the behavior of other fields.

It is always advantageous to bring the gas into the compressor station by piping it into both ends of the intake gas header so that each compressor will receive about the same load of gas. If the gas header is unusually long it is sometimes necessary to bring one of the incoming trunk lines into the center of the header as well as into each end. As the trunk lines go out into the field they should become progressively smaller in size as various feeder or branch lines are brought into the main trunk line. This can best be shown by an illustration of part of a gathering system as in Figure 1.

By knowing the approximate volumes on each lease which feeds into the trunk line the size of each segment can be calculated through the use of Weymouth's formula by the trial and error method; that is, the pressure drop can be assumed to be proportional to the length of each line segment. Then by taking the total amount of gas feeding into each segment, the size of the respective lengths of pipe line can be calculated. Before the most economical size is determined, however, other assumed pressure drops should be made since it may not be the most economical plan to have pressure drops proportional to the distance through which the gas must travel. These calculations can not be made with too high a degree of accuracy because allowances must be made for the bringing in of new wells on each lease and also the possibility of securing gas from leases adjoining the trunk line on which con-

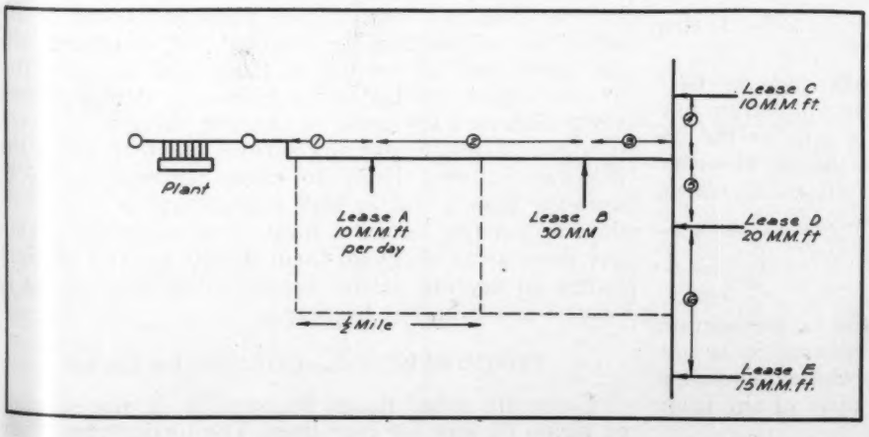


FIGURE 1

Part of a Gas Gathering System. Amount of Gas handled by Each Segment.

(1) 85 million cubic feet per day
(2) 75 million cubic feet per day
(3) 45 million cubic feet per day
(4) 10 million cubic feet per day
(5) 35 million cubic feet per day
(6) 15 million cubic feet per day

Pressure drop in each segment should be approximately proportional to its length.

tracts have not been made at the time the lines are laid. To take care of such contingencies, connections should be welded into the trunk lines at various points wherever it is possible that additional gas may be secured in the future. Block gates on trunk line loops often prove to be invaluable when certain sections of the field system must be shut down for repairs.

Weymouth's Formula is expressed by the following equation:

$$Q = (870)\, D^{8/3} \left[\frac{P_1^2 - P_2^2}{L}\right]^{1/2}$$

where Q = Cubic feet per 24 hrs. at 14.4 lbs. and 60°F.
P_1 = Initial pressure lbs. per sq. in. abs.
P_2 = Terminal pressure lbs. per sq. in. abs.
D = Inside diameter of pipe in inches
L = Length of pipe in miles

The constant in the formula is based on gas of 0.6 specific gravity. For gas of other specific gravity the constant becomes $870 \left[\frac{0.6}{G}\right]^{1/2}$ where G is the new specific gravity.

From this equation nomographic charts have been made so that slide rule calculations are no longer necessary. The engineer however should verify the results he finds on such charts by actual calculations.

RELATIONSHIP BETWEEN SIZES OF THE SUCTION AND DISCHARGE LINES

In laying out a gas gathering system, there should be a definite relationship or balance between the sizes of the suction and the discharge lines serving a compressor station, i.e., the amount of horsepower expanded in pulling the gas to the station should be no greater than the energy required to force the gas from the booster station to the absorption plant. The flow of gas through field lines is essentially isothermal, therefore the work required to handle a fixed quality of gas at a certain temperature is proportional to the logarithm of the ratio of the higher to the lower pressure. This fact is easily seen by reference to the equation for the isothermal expansion of a perfect gas:

Work per lb. mol of gas = $R\ T\ \ln_e P_1/P_2$
where R = Ft. lbs. per °F per lb. mol = 1544
T = 460 + °F
ln = Natural logarithm base (e)
P_1 = Initial pressure lbs. per sq. ft.
P_2 = Terminal pressure lbs. per sq. ft.

If the average pressure on the oil-gas separators in the field is 5 pounds per square inch gage and the suction to the compressor is atmospheric the ratio of P_1 to P_2 would be $\frac{5 \text{ lb} + \text{atmos. pr.}}{\text{atmos. pr.}} = \frac{19.7 \text{ lb abs}}{14.7 \text{ lb abs}} = 1.34$. If this same gas is compressed to 50 pounds gage or 64.7 pounds per square inch absolute, the discharge line would consume the same amount of energy as the intake line if the terminal pressure at the oil absorber were 48.3 pounds per square inch. In other words

$$\frac{19.7}{14.7} = \frac{64.7}{x}$$
$$x = 48.3$$

The importance of pressure differential in the suction lines is therefore often overlooked because it is not the pressure drop which determines the expenditure of energy, but the logarithm of the ratio of the inlet and terminal pressures of the line.

INCREASING GAS-HANDLING-CAPACITY OF A COMPRESSOR STATION

Additional gas occasionally is tied into a gas gathering system. The increase in gas volume often calls for either parallel trunk lines or more compressor units in order to maintain the desired pressure on the leases from which the gas is being purchased. The solution of such a problem is more complicated than one would consider it to be on first thought since the compressor station and its suction and discharge lines are interdependent. If the compressor station is enlarged with no change in the field lines, the pressure differentials through the pipe lines increase, causing a decrease in the amount of gas handled per compressor unit. Likewise, enlargement of the field lines is poor economy if the compressor station cannot handle the amount of gas fed to it. There is this much to be said in favor of enlargement of the field lines, namely, that the cost of operating and maintaining the lines is far less than compressor upkeep. Therefore it would be preferable to spend a definite amount on field lines to obtain a certain increase in gas handling capacity than it would be to invest a similar sum in compressors to get the same result.

ADVANTAGE OF LARGE LINES OVER SMALL ONES

If it appears likely that a gathering system will have to be enlarged in the near future it is good economy to install a larger line instead of putting in the proper size line at the time, and a parallel one later on.

For example a 12-inch I.D. line will handle 5 percent more gas than an eight-inch line and a 10-inch line operating in parallel.

This result is obtained from Weymouth's formula by taking the (8/3) power of the diameter of the line, since the quantity Q, is proportional to that power of the diameter.

$$12^{8/3} = 750 \text{ or } \begin{cases} 8^{8/3} = 257 \\ 10^{8/3} = 457 \end{cases}$$

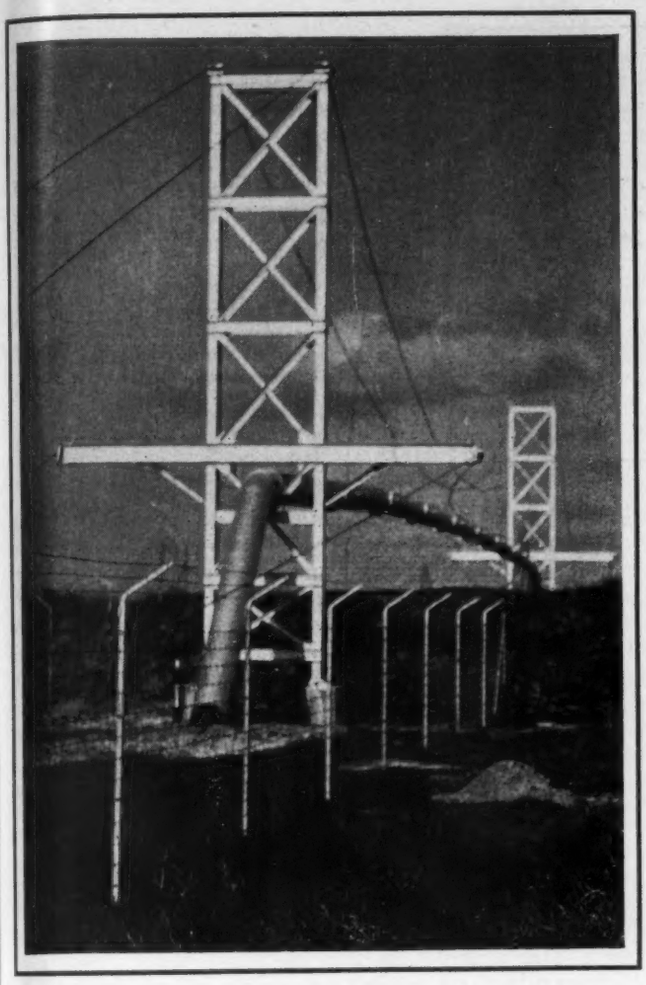
$$\frac{750}{714} = 1.05 \text{ Ratio of Capacity of } \frac{\text{12-inch line}}{\text{8-inch + 10-inch lines}}$$

RIGHTS OF WAY

Several proposed gathering systems should be mapped out by the engineering division before an attempt is made to secure rights of way. By having several different plans, a comparison of right of way costs can be made; for example, a saving in the number of feet of trunk line may be obtained by laying the line diagonally across a farm. But this increased saving may be offset by the additional cost of crop damages as well as the added cost of policing the diagonal line, compared with the simple task of keeping in touch with the condition of lines which are laid along highways. Although lines along highways are easier to observe, there is, however, this disadvantage that any serious gas leak along the highway is more likely to cause personal injury to someone than a similar leak might cause if it were on the line running across a farm. It is advisable to keep gas lines away from all farm dwellings and oil field camps on account of the danger of the loss of life in case of fire from line breakage.

TOPOGRAPHICAL CONSIDERATIONS

There are other things to consider in the selection of rights of way for pipe lines. The topography of the



land should be taken into consideration as well as the nature of the soil. Excavation costs through rocky land may be as much as two or three times the cost of digging ditches through ordinary soil or clay. If the proposed line can be kept away from areas where water stands, rapid external corrosion of the pipe lines often can be prevented.

RIVER CROSSINGS

It is well to avoid as many river crossings as possible, as floods are apt to wash out pipe line crossings unless they are placed on suspension bridges above flood level. Pipe lines can be laid in beds of streams with a fair degree of success if a semi-circular bend is made up stream, and the line is anchored heavily with river clamps so as to overcome the buoyancy of the water. By bending the lines upstream the force of the water tends to compress the joints of pipe whereas tension is set up, tending to pull the line apart if it is laid straight across the stream or is bent downstream. In Figure 2 a diagrammatic sketch shows the right and wrong methods of construction of river crossings. If the river has a changeable channel it is well to anchor the line for some distance on each side of the present river bed to take care of any future change in the bed of the stream. Changes in the channels of broad, meandering rivers having quicksand bottoms often come about suddenly during flood stages. Several parallel lines should be laid across the stream, so that the main line would not have to be shut down in the event one line should break. Each parallel line is equipped with a shut-off valve on each bank of the river. The capacity of the several parallel lines should be greater than the main line so that the breakage of one line would not cause the remaining lines to become a bottle-neck, or constriction for the trunk line.

Since the gasoline plant is not considered a common carrier, it can not exert the right of eminent domain and confiscate the land across which the trunk lines of the gathering system may cross. It does have the right, however, to lay the gathering lines on individual leases provided a reasonable payment is made for crop damages. In some districts where unreasonable demands have been made for right of way costs some companies have even gone so far as to spend greater sums in laying pipe lines around certain tracts of land rather than to set the example of paying exorbitant right of way costs. The question of rights of way should be handled by competent legal talent and not by the engineer. Of course it is necessary for the engineer and attorney to work together in securing the most suitable location but the main thing is to see that the right of way is obtained before any entrance is made upon a tract of land for the purpose of starting the construction of a pipe line.

The right of way generally calls for a certain width through a tract of land. For example, if it is in a heavily forested region it may be necessary to clear away trees and brush for a width of 20 feet or more in order to haul in the material and carry on the work of ditching, laying the pipe and finally back-filling the

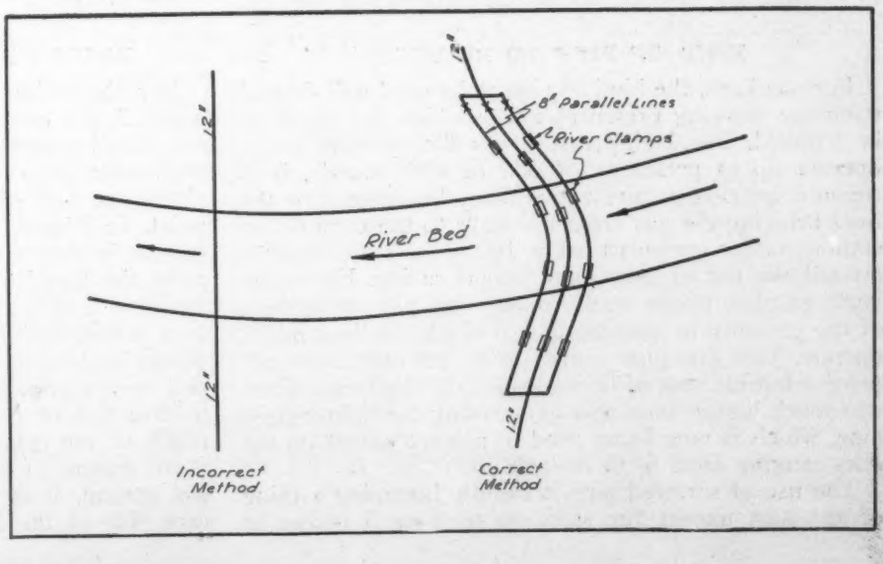


FIGURE 2

Correct and Incorrect Methods of Installing River Crossing in a sandy river bed too wide for a suspension bridge.

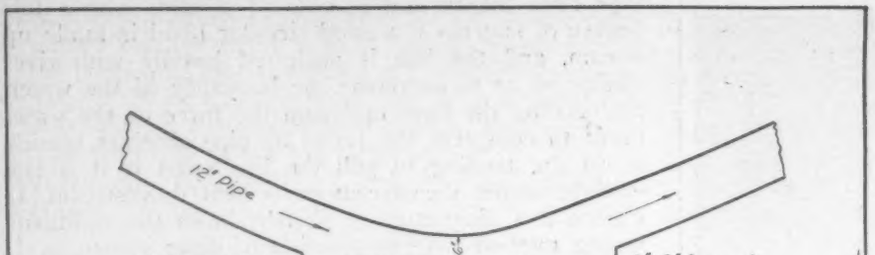


FIGURE 3

Diagrammatic Sketch showing location of drip connection in a low place in the line.

ditch. In good farming areas it is not so essential to use such a wide strip of ground, for once the line is laid the farmer may go ahead and plant crops in the soil above the pipe line, unless regular inspection of the particular line is considered essential in the operation of the gathering system.

Most right of ways provide for the right of ingress and egress, i.e.: in case of line breakage or whenever repairs are needed the pipe line owner has the right to enter and leave the particular tract of land. Of course settlement may be required in the event of crop or property damage.

CONSTRUCTION OF PIPE LINES

As soon as the rights of way have been obtained, the construction of the pipe lines is the next step in the bringing of the gas to the plant. This work may be done either by an organization of men within the oil company or it may be contracted with some outside engineering firm which specializes in pipe line construction. The tendency has been toward the letting of more and more contracts to contractors. Although at first one would think that an organization within a company might put in a line more economically than a contractor, the opposite results have been found to be the general rule. This is due probably to the fact that an oil company cannot afford to maintain a pipe line crew from one month to another, while the contractor is able to keep an experienced crew at all times. In addition to this, the contractor usually has all kinds of labor-saving machinery which many oil companies may not see fit to purchase just for occasional construction periods.

KIND OF PIPE TO BE USED

For gas lines, the kind of pipe to be used will depend upon the working pressures under which the gas is to be handled. For high-pressure gas lift systems which operate up to pressures of 500 or 600 pounds, it is common practice to use extra heavy line pipe. For the lines bringing the gas from the wells to the compressor stations under pressures below 100 pounds the trend is toward the use of very light weight casing. For many years gasoline plants used ordinary line pipe, regardless of the pressure or vacuum under which the lines might operate. This line pipe proved to be not only more expensive but the cost of laying, especially the larger sizes, was much higher than that of handling the light-weight pipe, which is now being used to a large extent on the lines ranging from 6- to 24-inch.

The use of screwed pipe is rapidly becoming a thing of the past except for sizes up to 2 or 3 inches in diameter, and in many cases even 2-inch lines are being laid with special flanged couplings instead of screwed couplings. For the larger lines the use of sleeve couplings on each joint is being replaced by the method of welding several joints together and placing a sleeve about every fourth or fifth joint. A number of the lines are of welded construction throughout their length. Expension is taken care of by special welded expension joints. If second-hand screw pipe is available it is often more economical to cut off the couplings, and either weld or couple the line with sleeves than it is to screw the pipe together with tongs.

THE REMOVAL OF LIQUID FROM THE LINE

The efficient operation of any gas line depends largely upon the degree to which liquid is kept out of the lines. The removal of the crude oil, water, and gasoline condensates cannot be accomplished unless adequate scrubbers and drips are provided. Every low place in each line offers a place for liquid to accumulate, thereby reducing the capacity of the line. If there is danger of certain crude oil flow tanks and separators failing to take care of large producing wells, the installation of scrubber tanks equipped with liquid-level traps is essential. Where the gas velocity is high, only the slowing down of this velocity will give the entrained mist a chance to settle out. In some cases separators, packed with glass wool, are required for the precipitation of very fine mist particles. These scrubber tanks generally are placed above the surface, in order to save the expense of burying the tank, and also to avoid the more rapid corrosion from the soil.

DRIPS FOR CONDENSATE REMOVAL

For the ordinary sags in the gathering lines, drips generally are used for the removal of liquid. These drips are placed a short distance on the down-stream side of the lowest place in the line, usually at a point which is about one half of the pipe diameter above the lowest point. In Figure 3 the proper location of a drip connection is shown. If the drip were placed at the lowest point the liquid accumulating beyond this point would not have a chance to run back freely into the drip and as a result, within a short time, a large slug of liquid would be surging back and forth on the down stream side of the drip. If there is a likelihood of the reversal in direction of flow of the gas in a main line, as the result of the enlargement of one plant and the partial abandonment of another station operating on the same gas system, it is well to provide drip connections on each side of the lowest place in the line. The swaged

nipple into which the condensate drains should be at its upper end, half the diameter of the line for 8-inch and above, in size, and the same size as the diameter for 2- to 4-inch lines. Since drips are expensive to install and increase the operating cost required to keep the lines free of liquid, the grading of the bottom of the pipe line ditches should be made with the view of eliminating as many swags in the line as it is economically possible. Figure 4 gives diagrammatic views of two typical drip assemblies. Part A shows a drip where dry pressuring gas is available while part B displays one which has to be drained by gravity.

The conventional drip usually is made out of a joint of pipe or casing, its size varying with the amount of condensate to be stored between drip blowing periods. So long as the gas line is under three pounds per square inch pressure or more, the drips can be readily emptied by opening the outlet valves. When the pressure in the line falls below the hydrostatic head of the condensate, it is necessary to shut the valve between the drip and the line, and then blow the condensate out with residue or high-pressure gas. When residue lines are not available the only alternative is to drain the drip. In level country a bell hole must be dug to a depth greater than the outlet of the drip. Such holes should be fenced in securely in order to prevent likestock or children from falling into them. If the condensate in the lines is not worth collecting as drip gasoline, it should not be allowed to accumulate or drain into streams causing damage to growing crops or injury to livestock.

RESIDUE RETURN LINES

The natural gasoline fractions are removed from the raw gas in the absorber, and the dry residue gas is returned to the producing leases to be used as fuel. It is customary to lay these fuel lines alongside the raw gas lines in order to save ditching costs, and to provide the needed pressure for blowing condensate from the drips connected to the raw gas lines. The residue gas often carries considerable quantities of water and absorption oil mists, which may be carried for a mile or more before they settle out and drain into the drips. Scrubber tanks placed a few hundred yards away from a plant on residue lines often prove effective in collecting water and absorption oil; thereby preventing freeze-ups in cold weather. When a residue line is laid in the same ditch with a raw gas line it is advisable to place the lines at least a foot or two apart so as to facilitate repair work and to reduce the tendency for electro-chemical action to take place, due to potential differences in the electro-motive forces of the two lines. The small valves which are used in the pressure lines to the drips should be kept in good condition, for otherwise residue gas will leak continuously from the fuel line back into the raw gas system. This leakage would not only tend to overload the compressors but would reduce the extraction efficiency of the plant in general, on account of the reduction in the gasoline content of the gas.

The natural gasoline manufacturer returns the residue gas to the edge of each lease from which the raw gas is purchased. From this point the oil producer pipes the dry gas over the lease. The usual contract calls for the return of sufficient fuel for lease operation. During the flush gas periods, the fuel question rarely causes any disputes or difficulties between the plant operator and the oil producer. In the older fields the matter of distributing fuel gas is indeed a major consideration in the operation of the plants and leases. Wasteful practices of all kinds have to be stopped, such as the use of flambeaus or torches for out-of-door illumination. Diaphragm reducing valves replace gasometer cans around gas engine houses. Residue meters also are placed on each lease to measure the return gas. These steps toward conservation must be taken to assure each lease sufficient fuel, especially during the early morning hours when the demand for dry gas is heavy, and the plant is receiving its minimum supply of raw gas. In many of these older fields an effort is made to equalize the demand for fuel by pumping the wells on the several leases supplying the plant at different times during the day and night. This arrangement gives the plant a steadier load of raw gas. Such cooperation is difficult to obtain, however, because it is only natural that lease operators would prefer to pump their wells in the day time.

Whenever the gas volumes become extremely low and the gasoline content of the gas runs 10 gallons or more per thousand standard cubic feet, the amount of residue gas left after plant extraction sometimes is hardly enough to run the engines at the gasoline plant. In such fields it is necessary either to buy residue gas from some other field, or to resort to the use of Diesel engines and oil-fired boilers. The propane and butane fractions from these plants are usually carbureted with air and used as fuel in the field, this practice being more economical than that of selling those fractions in tank car lots to some distant market.

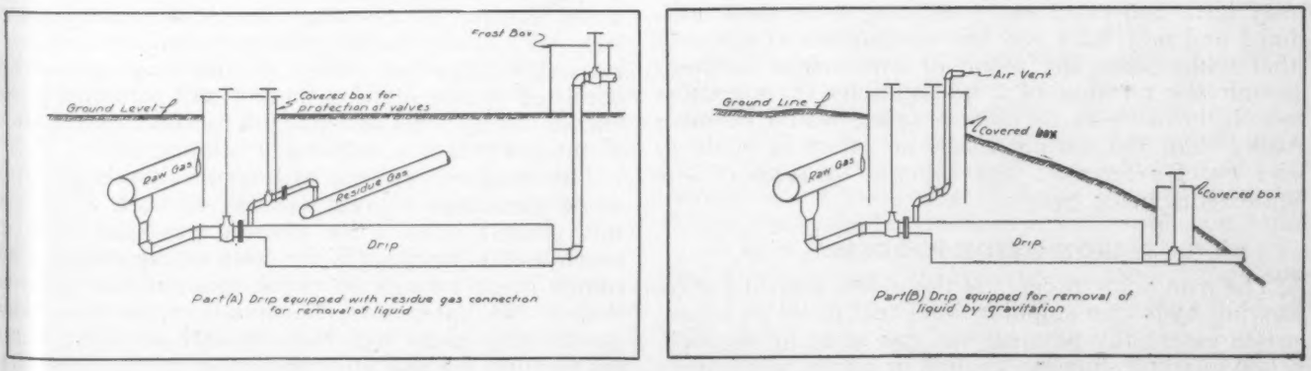


FIGURE 4

Diagrammatic drawings of two types of drip assemblies.

Cleaning High-Sulphur Gases

MICHAEL J. LEAHY
Consulting Engineer

THE problem of removing hydrogen sulphide and other sulphur compounds from fuel gases is one of great importance to the natural gas industry, the oil refiner and the manufacturer of carbon black.

Prior to the extensive use of cracking equipment in refining oil, the installation of hydrogenation and polymerization processes and the passage of laws prohibiting the wastage of natural gas, it was customary to separate all high-sulphur gases from the products being manufactured and then to burn such gases in torches. It is well known that high-sulphur gases may not be used in hydrogenation processes or for polymerization, that the presence of such gases in cracking apparatus is ruinous to such equipment, and that natural gas containing even small amounts of hydrogen sulphide will not produce carbon black of high quality. Thus the problem of cleaning such gases has reached a critical stage due to the factors mentioned and hence an outline of various methods of treating, or cleaning, high-sulphur gases is timely.

The writer has spent more than nine years working on methods of treating gases containing hydrogen sulphide; has collected a library containing more than 650 United States and foreign patents and over 480 literature references relating to processes and methods of removing hydrogen sulphide from gases; has conducted numerous experiments with practically every known gas-treating process; has built and operated pilot-plants for testing a number of such processes; and has built and operated a commercial treating plant in which free sulphur may be produced as a by-product of cleaning such gases. The following outline of individual processes is compiled from the cited data and from the author's personal experience with such processes. Other investigators may have had experiences differing from those outlined and may have reached conclusions at variance therewith. Since the scope of this article will not permit the printing of a bibliography of references which, in order to be of real value, would be more bulky than the outline itself, no effort is made to cite exact references and patents to support any statements made herein.

THE accompanying discussion of methods and processes for cleaning high-sulfur gases is most timely because of present interest in that problem among refiners and gasoline plant operators. In this article Mr. Leahy has reviewed several processes and traced their development. The article has been reviewed by certain interested people in this country interested in the development of gas purification processes and remains virtually unchanged from the original writing. The statements given, however, are strictly those of the author and the views expressed are his own and are not to be construed as approved or sponsored by *The Refiner*. Further, the subject is not closed with this publication and if there be further technical or engineering information available for publication due consideration will be given it.

IRON OXIDE PROCESS

The iron oxide process is the oldest known for removing hydrogen sulphide from fuel gases and comprises essentially passing fuel gas over, or through a bed of wood shavings coated, or mixed, with finely divided iron oxide such as bog-iron ore. The hydrogen sulphide contained in such gas reacts with the iron oxide to form ferrous sulphide and water. After about one half the available iron oxide has thus been converted, the mixture of shavings, iron oxide and ferrous sulphide is exposed in shallow piles to the action of the air. Atmospheric oxygen reacts with ferrous sulphide to precipitate sulphur and to regenerate iron oxide, thus rendering the material fit for re-use.

At the time this process was first developed, the only fuel gas used was artificial gas which contained not more than 0.3 percent hydrogen sulphide. Even with this type of gas it was found that excessively large contactors were required because of the fact that the iron oxide had to be relatively dry to prevent caking and hence large surfaces coated with very thin layers of the oxide were needful to obtain proper contacting of the gas. Further, large areas were required for aerating the spent treating material. Also, while changing the trays in the contactors relatively large quantities of air were necessarily admitted to the interior thereof and sometimes this excess of air in the fuel gas led to violent explosions in the gas mains or in the gas holders.

The reaction between hydrogen sulphide and iron oxide generates a great amount of heat. Hence, if this process is used for treating gas containing as much as 1 percent H_2S, the heat of the reaction becomes great enough to cause spontaneous combustion in the contactors. For instance, an iron-oxide gas-treating plant was built in 1927 in West Texas for treating natural gas containing 4.6 percent H_2S. This plant was operated for about four hours at which time it caught fire and was destroyed. This was caused by the intense heat produced by the reaction between the hydrogen sulphide and iron oxide.

The iron-oxide process is unsuitable for treating large volumes of natural gas containing high percentages of H_2S on account of the high cost of the iron oxide required; the impossibility of removing spent materials from, and adding fresh materials to the system without contaminating the gas with air; the impossibility of controlling the temperature and the rate of the reaction; the excessive cost of compressing the gas sufficiently to force it through the iron-oxide-shavings mixture; and the bulky and expensive equipment required.

IRON HYDROXIDE SUSPENSIONS

Attempts were made to overcome some of the disadvantages of the iron-oxide process by using iron hydroxide in suspension in water. The foul fuel gas was contacted with this liquid and the reaction between the hydrogen sulphide and iron hydroxide occurred directly in the liquid. The spent liquid was then contacted with atomized air to oxidize the ferrous sulphide therein to iron hydroxide. What generally happened in practice was that the iron sulphide was oxidized completely to iron oxide and this iron oxide would not remain in suspension. Also it was found that the cost of the iron hydroxide was greater than an equivalent quantity of bog-iron ore. Likewise, the temperature of the reaction was susceptible to control to some extent; but a great deal of water was necessarily vaporized and this vapor (steam) later had to be removed from the treated gas to prevent condensation in the mains and holders. The writer has experimented with variations of this process in attempts to make it suitable for cleaning high-sulphur gases, but without success. It was condemned for many reasons; but mainly because of cost of equipment, high power costs, and finally, because the volume of air required for oxidation of the spent suspension was from three to eight times the volume of gas which could be treated.

THE FELD PROCESS

About 1911, Walther Feld in Germany developed a process for treating artificial gas containing hydrogen sulphide, ammonia, and cyanides. This process comprised passing such gas through a polythionate solution and then treating the solution in a separate container with sulphur dioxide.

Theoretically, this process seemed ideal, as hydrogen sulphide reacts with a polythionate to form a thiosulfate and to precipitate free sulphur. Thiosulfate should then react with sulphur dioxide to regenerate the polythionate. Hence the process should be cyclic in character in that sufficient sulphur should be formed during the reaction to burn to form sulphur dioxide for use in regenerating the polythionate. However, in practice it was found that the final products were ammonium sulfate, thiocyanates, and thionic acids. Any free sulphur which could be separated was highly acid in character and so impure that it could not be burned in any known type of sulphur burner. However, the Feld process came into general use in the artificial gas industry mainly because ammonium sulfate—a valuable by-product—could be made therein in a very pure state. Also the equipment required for treating a given volume of gas by the Feld process was much simpler and less expensive than that required in the iron-oxide or the hydroxide processes.

The writer experimented in the laboratory with many variations of the Feld process for treating natural gas containing as much as 6.5 percent H_2S. Later, a pilot-plant capable of treating 55,000 cubic feet of natural gas containing 6.1 percent H_2S was used for a lengthy test on such variations of the Feld process as had shown promise in the laboratory. It was found that no matter what the rate of flow of either the gas being treated or the solution, the solution temperature, the concentration of polythionate in the original solution, the percentage of polythionate remaining in the foul solution, and other factors were, only about two-thirds of the total hdyrogen sulphide in the gas could be removed. The sulphur recovered contained much thionic acids and sulfites and hence was of little value. In this connection it is well to point out that natural gas in the Permian Basin which contains much hydrogen sulphide also contains high percentages of carbon dioxide. At least, after testing hundreds of oil and gas wells in that district for total gas volume, percent H_2S, percent CO_2, and gasoline content, using the method developed by the writer[1], it was concluded that all Permian Basin natural gas contained appreciable amounts of carbon dioxide.

It is probable that the presence of this carbon dioxide in the gas had some bearing on the efficiency of treatment when using the Feld process. Other serious objections to the use of the Feld process for treating high-sulphur natural gas are the intense corrosive action of thionic acids on the metal parts of the equipment and the difficulty of filtering the sulphur formed from the solution; so that the solution may be re-cycled. It was found that this type of sulphur formed an almost impervious layer on the filter cloth and that this layer could not be removed completely. Furthermore, polythionate solutions necessarily contain some free sulphur dioxide and hence, if such solutions are contacted with fuel gas from which practically all the H_2S has been removed, such gas will become contaminated with sulphur dioxide and must therefore be washed with large volumes of water to remove this impurity.

SODA-ASH PROCESS

At practically the same time that Feld was developing his process, numerous investigators were working on processes ultilizing soda-ash solutions for removing H_2S from artificial gas. The best known of these processes is the Seaboard process in which a solution containing about 5 percent commercial soda-ash is brought into contact with the fuel gas in counter-current flow. The soda-ash solution absorbs hydrogen sulphide from the gas. The treated gas is separated from the foul solution and this liquid is then sprayed into a tower through which air is being forced in an upward direction. Hydrogen sulphide contained in the solution mixes with such air and this mixture is blown out the open top of the tower. The H_2S-free solution is then used for absorption of further amounts of H_2S from the fuel gas.

This process is very successful when used for treating gases containing but traces of H_2S. However, when used for treating high-sulphur natural gas, it was found that the rate of circulation of the solution had to be very high, the amount of air required to sweeten the fouled solution was extremely

[1]Rapid Method of Testing High-Sulphur Gases. Refiner & Natural Gasoline Mfgr., Vol. 8, No. 10. M. J. Leahy.

high, and the amount of fresh soda-ash which had to be continuously added to the solution to keep it at its most efficient strength was excessive. Further, the corrosion of metal parts of the equipment was rapid. However, probably the greatest objection to the use of this process in the high-sulphur gas area lies in the fact that all hydrogen sulphide removed from the gas was blown into the air and hence produced a nauseating and poisonous atmosphere for some distance surrounding the treaters. No useful by-products were obtained from the use of the soda-ash process. While it is true that sodium thiosulfate gradually forms in the solution, no method of recovering this thiosulfate has been devised.

Several commercial units operating on the soda-ash process have been used for treating small volumes of sour natural gas so that such gas may be used in gas engines in the oil-field. One large gas company is using a modification of the soda-ash process for treating large volumes of natural gas which contains but traces of H_2S. This gas is treated under pipe-line pressure (about 450 pounds per square inch) in order to increase the partial pressure of the H_2S contained therein and thus effect more complete absorption and to obviate the necessity of recompressing the treated gas. This causes the solution-circulating costs to be excessive, but apparently the total costs of treating are not excessive; for the company still continues to use the method.

GIRBOTOL PROCESS

The Girbotol process for purification of natural gas and removal of hydrogen sulfide, has been developed in the past few years and is now coming into commercial use. This process and the applications thereof in industry was very ably decribed by Dr. R. R. Bottoms and W. R. Wood of The Girdler Corporation in The Refiner under the title "The Girbotol Purification Process," issue of March, 1935, page 105.

THE LEAHY PROCESS

After experimenting with the use of a solution of sulphurous acid for the absorption of H_2S from natural gas, the author became convinced that the proper procedure was to reverse the above cycle by absorbing H_2S in water and then contact this water solution of hydrosulphurous acid with sulphur oxide gases. This was done with the result that there was obtained a water solution containing traces of both H_2S and SO_2 and a considerable quantity of very finely divided sulphur in suspension.

Further experiments showed that the sulphur in suspension could be flocculated by the addition of certain soluble electrolytes, and that such flocculation caused the suspension sulphur to settle rapidly. However, after the clarified solution was decanted and then used for absorption of further quantities of H_2S, it was found that the pressure of the soluble electrolyte serving as a flocculating agent reduced the volume of H_2S possible to absorb and the rate of such absorption. Finally, another class of electrolytes capable of increasing the volume and the rate of absorption of H_2S was tested by adding one or more of such to the solution which already contained the flocculating electrolyte.

Experiments were continued with this type of treating solution with some startling results. The volume of H_2S absorbed by such a solution and the rate of such absorption were increased greatly. Further, after treatment of the foul solution with sulphur oxide gases, the sulphur formed therein flocculated rapidly and settled to the bottom of the solution container; thus permitting decantation of the clarified solution. It was found also that this type of solution could be re-cycled indefinitely without decreasing its efficiency.

After drying, the sulphur so recovered was found to be very finely divided and neutral in character. That is, it was neither highly acid nor alkaline. Another characteristic peculiar to this type of sulphur was that when sprayed or dusted on trees or vegetables it clung tenaciously thereon and was not washed away by heavy rains. This sulphur was also extremely light, weighing but 28 pounds per cubic foot when dry. Hence it would float on water for some time before going into suspension. But when pure water was used for making such a suspension, the sulphur would not flocculate until a flocculating electrolyte was added to the water.

It was found by further experimentation that if a solution containing but a small amount of the flocculating agent and a large proportion of an electrolyte which in itself had value as a fertilizer, was used as a gas-treating solution, a prepared fertilizer compound containing sulphur could be recovered in solid form. It was found that prepared fungicide and insecticides could likewise be recovered from treating solutions by choosing the proper electrolytes which had either fungicidal or insecticidal properties and using concentrated solutions of such compounds. It may be well to state here that these processes, and the apparatus used therein, are fully protected by patents issued to the writer and which include U. S. Patent No. 1,800,892, U. S. Patent No. 1,812,795, U. S. Patent No. 1.995,545, U. S. Patent No. 2,026,840, January 7, 1936, and others pending.

A small company was organized for the purpose of commercializing these processes and this company built and operated a gas-treating plant capable of treating three million cubic feet per day of natural gas containing 9.2 percent H_2S. An illustration of this plant in operation is shown in Figure 1. The plant is located in the Gulf-McElroy oil field in

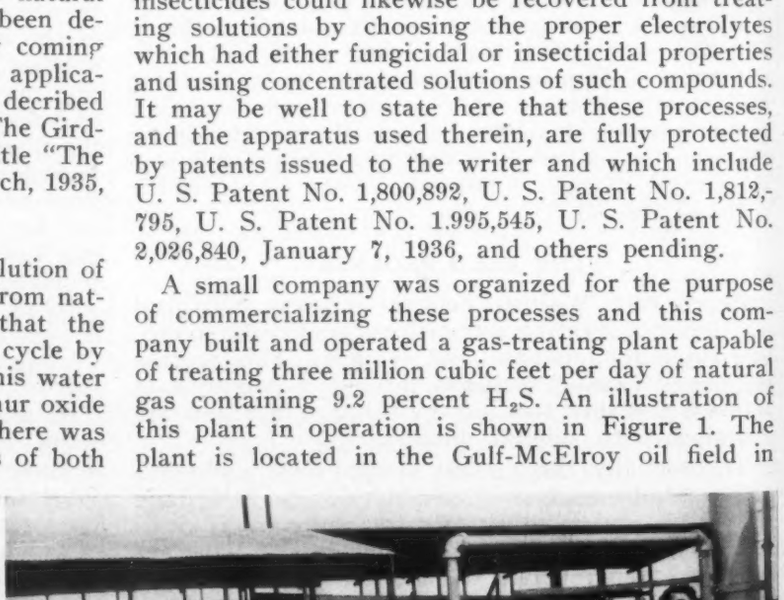


FIGURE 1

Gas treating plant in operation processing three million cubic feet of gas daily.

FIGURE 2
Pilot plant for testing gas treating processes.

West Texas. Figure 2 shows one of the pilot-plants erected and operated for the purpose of testing these processes on a different type of gas.

While this large gas-treating plant was constructed and operated for recovery of sulphur primarily and thus no special efforts were put forth to treat the gas completely, it may be stated that the gas could be treated in one passage through the plant to a hydrogen sulphide content of less than 0.1 percent.

Some data relative to the operation of this treating plant may be of interest. The untreated gas entered the plant at a pressure of about 30 pounds per square inch. The pressure of the treated gas was about 21 pounds per square inch. This seems to be a rather large pressure drop through the system; but it should be remembered that the volume of the gas was reduced by about 9 percent due to the absorption of the H_2S content. Hence the loss in pressure due to friction was relatively small.

In order to treat this volume of gas, solution was circulated at a rate of about 150 gallons per minute. About 200 gallons of make-up water per day was required. No steam nor other means of heating the treating solution was necessary. Neither was any cooling required. In fact the process has been operated in the open when the atmospheric temperature was minus 5° F. without noticable decrease in the efficiency of treatment. Sulphur oxide gases were of course, obtained by burning sulphur in a pressure-type sulphur burner. These hot gases were immediately contacted with the foul solution and thus kept the solution at a practically uniform temperature of 85° F. regardless of the atmospheric temperature.

Incidentally, when the process is operated for the production of pure sulphur as a by-product, the treating solution will last indefinitely and hence the cost of chemicals is practically nil. However, when prepared fungicides, fertilizers, or insecticides are being produced as by-products, additions to the solution of the proper electrolytes are required in order to keep the solution fully concentrated and to provide for replacement of quantities of the prepared compounds which are continuously separated from the treating solution.

The total power required to operate this plant (electric motors were used) was 11 kwh. Further, the plant could be completely controlled by the manipulation of one control valve. Hence one man could operate the plant successfully. However, two men were on duty at all times and efficient gas masks were kept ready for instant use. A gas containing such a high percentage is extremely poisonous and a deadly concentration of H_2S in the air seems to paralyze the olfactory nerves almost instantly; therefore the sense of smell is of but little value in detecting lethal concentrations. This is the reason why two operators were on tour at all times so that if a break in the plant should occur which would place one operator in danger, the other could quickly don a gas mask and rescue his comrade.

The sulphur produced in this plant was extremely finely divided. In fact the average particle diameter was less than one micron (0.000039 inch); hence it could be classed as truly colloidal in nature. Further, the sulphur actually produced and sold, after being air-dried, was 98.6 percent pure. It had a property that is characteristic of all finely powdered sulphur and that is it caused excessive lachrymation if the powder was dusted into the eyes. However, no permanent injurous effects on the eyes of operators could be found even after months of exposure to the sulphur dust. However, it is a fact that for about 10 minutes each day each operator would lachrymate so copiously that he would be almost blinded by his own tears.

The sulphur produced at this plant was sold directly as a fungicide. In order to overcome the objection which was made that there was a possibility that the market could not absorb all of this type of sulphur which could be produced in West Texas, the author perfected processes for using finely divided sulphur and finely divided carbon to produce carbon disulphide[2]. By the use of this process for the production of free sulphur as a by-product from treating high-sulphur gas and the use of such gas for making finely divided carbon, sour natural gas from wells far distant from markets available for disposal of the treated gas as fuel may be completely and profitably utilized for the production of carbon bisulphide for which there is always a ready market.

The Leahy gas-treating process is economical in that no heating or cooling of the treating solution is necessary. No air is needed for regenerating the foul solution. No hydrogen sulphide is released to the atmosphere to create a nuisance. The process does not require complicated and costly apparatus for operation and may be easily controlled. There is a wide range between the over-activation and under-activation of the treating solution and hence close analytical control of the process is unnecessary. When producing pure sulphur as a by-product the cost of chemicals is negligible. Power costs are very low. Valuable products other than the treated gas are obtained.

[2]Advances in Utilization of Waste Natural Gas. Petroleum Engineer, Vol. 6, No. 9. Michael J. Leahy.

UTILIZATION OF . . .

Petroleum Coke

D. GLYNN JONES, A.I.C.*

INSTALLATION of a coking plant is usually justified merely by the enhanced profits derivable from low value residue by its conversion into gasoline, gas oil and other derivatives. Petroleum coke, which is the end profit of the process, is however, far from being valueless and can often be sold at a good price. The accompanying article is a compilation of some of the purposes for which petroleum coke is suited.

THE main use of petroleum coke is as a fuel, either in the form of lumps or in the pulverized condition. When used in lumps it suffers from certain disadvantages as for instance its low volatility, making it difficult to ignite. Furthermore, its low ash content does not allow of the formation of a protective layer of ash on the furnace bars, which are consequently exposed to the full heating effect of the burning fuel[1]. It has been stated[2] that even a coal containing 3 to 5 percent of ash entails high maintenance costs for the grate; a petroleum coke therefore, containing 1 percent or less of ash would involve even greater expense. In practice this difficulty is readily overcome by mixing petroleum coke with an equal amount of coal. It is probable that the major part of the petroleum coke produced in the United States is used in this form. When supplied in graded sizes the price of the combination is almost equal to that of anthracite coal. In an article by Campbell[3], a simple method of overcoming the low ash content is suggested in the provision of a clinker bed of about ¾-inch thickness or alternatively a layer of broken bricks in cubes of about 2 inches may be used. In this article details are also given of lighting and controlling household furnaces consuming petroleum coke. The present trend is for the use of petroleum coke as a domestic fuel to increase. In fact, so materially has this demand grown that comparatively little is left for actual plant consumption[4].

In addition to its use in lump form, a number of installations burning pulverized petroleum coke are reported as being in operation in North America[5,6,7]. For successful combustion pulverized fuel requires that 95 percent of the product shall pass through a 100 mesh and 85 percent through a 200 mesh screen[8]. This degree of fineness can easily be attained with a ball mill type of pulverizer, particularly if working in a closed circuit with an air classifier. Braunholtz[9] states that the inclusive cost of pulverizing to this specification is 18d to 21d (36c to 42c) per ton. Pulverized fuel possesses in many respects the advantages of liquid and gaseous fuels such as flexibility and ease of manipulation. It gives a higher thermal efficiency than all but the most modern of mechanical grates. Its thermal efficiency is also enhanced by radiation from the innumerable small particles of fuel. The most efficient conditions for operating with pulverized fuels are generally considered[10] to be 12,000 to 18,000 B.t.u. per hour per cubic foot of combustion space, i.e. from 0.8 to 1.2 pounds of pulverized coke per cubic foot of combustion space.

Petroleum coke has been used to some extent in briquetted fuels[5,10]. Coal tar pitch or asphalt are commonly used as binders, in the proportion of 8-10 percent of pitch of 170° F. softening point, or 6-8 percent of asphalt having 50-60 penetration[11]. Further details are given in a recent article by W. I. Jones[12]. The binder is smeared over the disintegrated particles by means of paddles at about 95° C. and the plastic mass pressed into briquettes at about 70-80° C. and pressures of about 2 tons per square inch are applied in 4 consecutive stages. There is a close relationship between the size grading of the particles and the consumption of binder, a powder of uniform particle size requiring much more binding material than one made of varying grades in which the fine material largely fills up the voids occasioned by the larger particles. The best grading is probably from 10 mesh to 200 mesh.

The application of petroleum coke to "colloidal fuels" is as yet an apparently undeveloped field, and one which offers considerable scope for development. A colloidal fuel prepared from fuel oil and petroleum coke possesses all the advantages of one prepared from coal and in addition others such as its cheapness, ease of pulverizing and freedom from ash. In the case of colloidal fuels containing suspended coal particles, the use of soaps, e.g. sodium stearate, is advocated as a peptizing agent[13]. Indications are not lacking that these bodies are also satisfactory for use in stabilizing "colloids" of fuel oil and petroleum coke. Among other stabilizing agents employed are: cork flour or ground cork bark[14] which is specifically claimed to be of value with pulverized coke; starch[15]; a gelatinizer and wool pitch wool fat or vaseline[16], calcium soaps and molten caoutchouc[17]. The Cunard patent[18] describes a liquid fuel consisting of a cracked fuel oil and coal dust pulverized so that all passes 180 mesh and practically all passes 200 mesh. It is claimed that the coal will remain in suspension without any additional stabilizing means. The Wyndham liquid-coal process[19,20] claims to maintain pulverized coal in suspension without the use of stabilizing agents. In this process, a bituminous coal with a low ash content is mixed with a fuel oil and fed through a series of roll mills. These bring about a size reduction so that 99 per-

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cent of the particles pass through a 200 I.M.M. mesh sieve. The most suitable proportion of coal and oil is 1:1. In another patent[21] Strevens and Hatfield prepare coal-oil mixtures by grinding the solid fuel to coarse colloidal dimensions in the presence of high boiling oil and 0.5-1.0 percent (on the weight of coal) of vulcanized or unvulcanized rubber. What has been successfully achieved in the case of coal-oil mixtures should not be difficult of accomplishment for coke.

Petroleum coke is used extensively for the manufacture of "electrodes," such as are employed in the aluminum industry[22,23], and in many other industries e.g. in the manufacture of steels, carborundum, graphite, calcium carbide, etc., employing electric furnaces of either the arc or resistance type. The use of petroleum coke for such purposes dates back for a number of years[24,25,26].

A typical analysis of petroleum coke as used for this purpose is approximately as follows:

Fixed carbon	90.0 percent
Volatile matter	7.0 percent
Ash	1.5 percent
Sulphur	1.5 percent
Water soluble salts (included in the ash)	0.75 percent

Such a coke as this requires further treatment to reduce the ash and volatile matter but cokes containing a maximum of 1 percent ash and 1 percent volatiles are considered sufficiently good for use without the elaborate treatment which follows. In order to reduce the amount of these impurities, the "run of still" coke is baked in either a vertical or horizontal kiln. This entails a loss of some 15 to 30 percent, depending on the type of kiln and the quality of the coke employed. If the volatiles are less than 1 percent originally, then the coke is merely dried to 0.1 percent of moisture. If necessary the coke is washed thoroughly to remove soluble salts. Following these operations the coke is reduced in size to between 8 mesh and 100 mesh, the sizing being done in such proportions as to produce a finished product having the highest possible density and the lowest porosity. Incorporation is then brought about with a binder (usually a hot blend of pitch and tar), and the mixture pressed into shape, being subjected to a final pressure of 2 tons per square inch. The compressed blocks are then calcined in kilns at a temperature between 1350° C. and 1600° C., the length of roasting varying from 6 to 21 days. It is stated that each ton of aluminum produced requires 0.6 to 1.0 tons of carbon.

A development making considerable progress in Norway is the Soderberg electrode, which is self-making[27]. In this process the electrode-forming paste is fed into a shell which is the vertical continuation of the electrode holder. As the electrode is consumed the mixture passes through zones of increasing temperature, up to a heating ring where final baking takes place. The normal furnace temperature of 950° C. has proved to be sufficient for this purpose. There are now said to be in operation Soderberg electrodes having a cross-section of 2.4 square meters.

It has recently been stated[28] that a coke containing less than 1 percent of ash and less than 0.5 percent of iron and silicon combined, derived from pulverized coal, is considered to be more suitable for the manufacture of electrodes than oil coke. However, in order to reduce the amount of ash in coal to this very low limit, a complicated flotation process is required. This separates "fusain" which, as well as being the lightest constituent of coal, contains most of the ash. It appears unlikely therefore that coke from "pure coal" will be a very serious competitor for petroleum coke except in certain special cases.

The important characteristics of a coke from the point of view of electrode manufacture are a very low ash content and a low percentage of volatiles. The first of these is governed very largely by the quality of the original crude petroleum. If this carries considerable amounts of silica, ferruginous compounds, etc., in suspension, or is produced along with edge water, then there will be a tendency for the residual coke to have a high ash content. The percentage of volatiles present in the coke will depend very largely on the type of coking installation employed and the conditions of the operation. A plant of a suitable type has been described[29], in which petroleum residues are coked in a continuous chain of containers, the nature of the final product being varied at will by altering the velocity of the containers through the coking chamber, or by changes in the operating temperatures.

Among other uses in the electrical industries for which petroleum coke is fitted may be mentioned the manufacture of carbon brushes, fillings for dry cells and bricks for electrolytic cells and furnace linings.

The use of petroleum coke for the manufacture of building bricks by mixing with a binder composed of cement and coke fines has been patented[30]. Petroleum coke is now being employed as a raw material for the manufacture of structural carbon[31] which is used in the form of bricks, raschig rings, or other special shapes. The raw material is crushed or ground to size, heated repeatedly at high temperature to eliminate organic matter and then blended with suitable organic plastic material such as tar or pitch. The plastic mass after moulding, extruding or other shaping operation, is baked at a sufficiently high temperature to decompose substantially all of the organic matter of the binder. The result is a homogeneous piece of practically pure carbon.

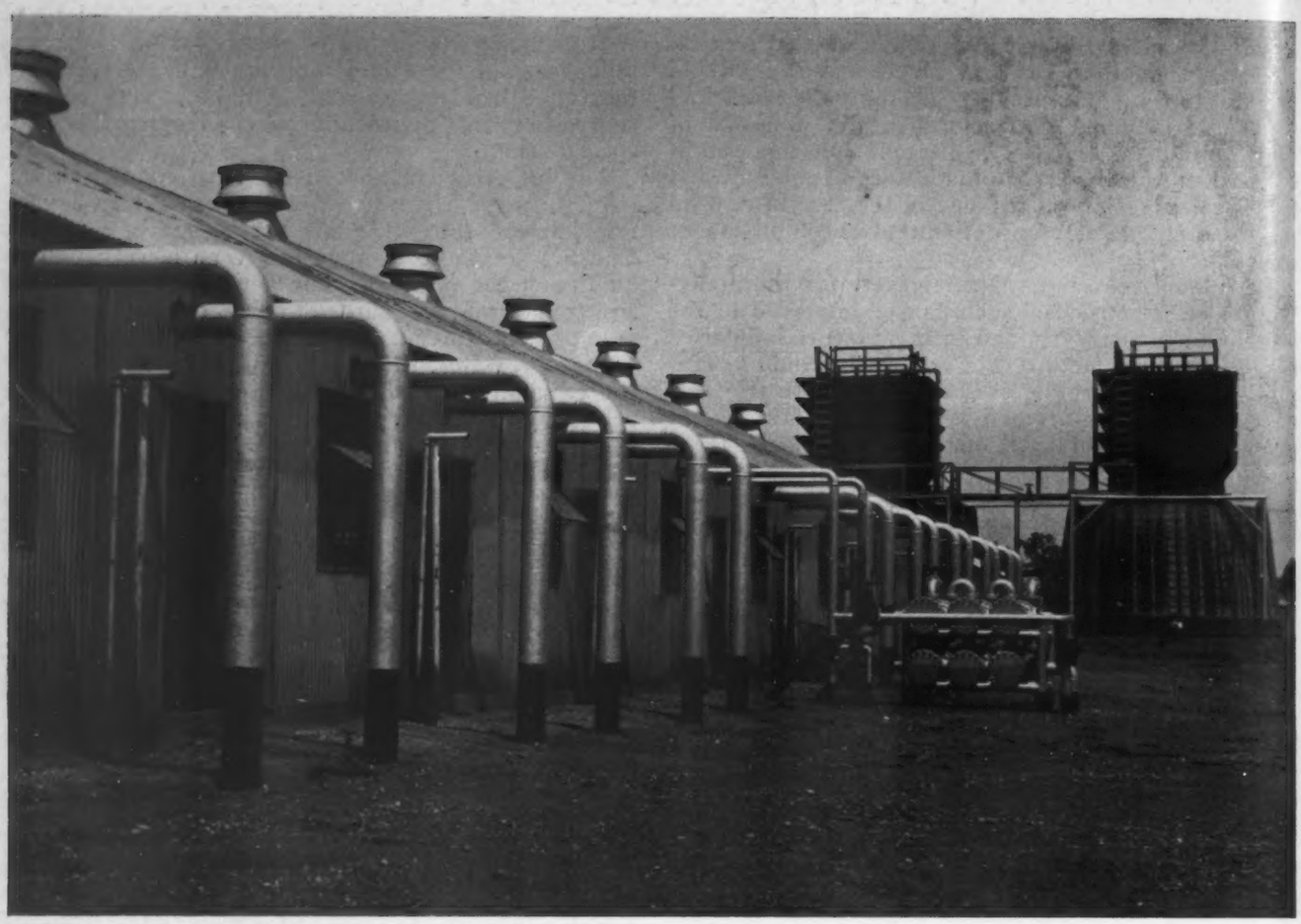
Petroleum coke has also been successfully employed as a raw material for the manufacture of activated carbon. Methods[32] consist in heating petroleum coke in the presence of lime and water to a temperature of 480° C. to 510° C., or in mixing petroleum coke with saw dust and acid sludge, followed by treatment with highly superheated steam. Another process claimed to yield 40 to 60 percent of activated carbon on the raw material has also been patented[33].

Petroleum coke can also be used as a metallurgical reducing agent. For this purpose it should have a low phosphorus content. Its suitability can be judged from the following quantitative analysis carried out on the ash of coke prepared by the method described in previous papers[29,34]. The ash formed approximately 1 percent by weight of the coke.

ANALYSIS OF ASH FROM PETROLEUM COKE

	Percent
Silicon	4.6
Iron	13.6
Aluminum (possibly contaminated by Tin)	1.6
Calcium	10.1
Manganese	0.3
Sodium (includes a small amount of Potassium)	7.9
Sulphur (calculated as SO_3)	33.2
Phosphorus	.034

(*Continued on page 284*)



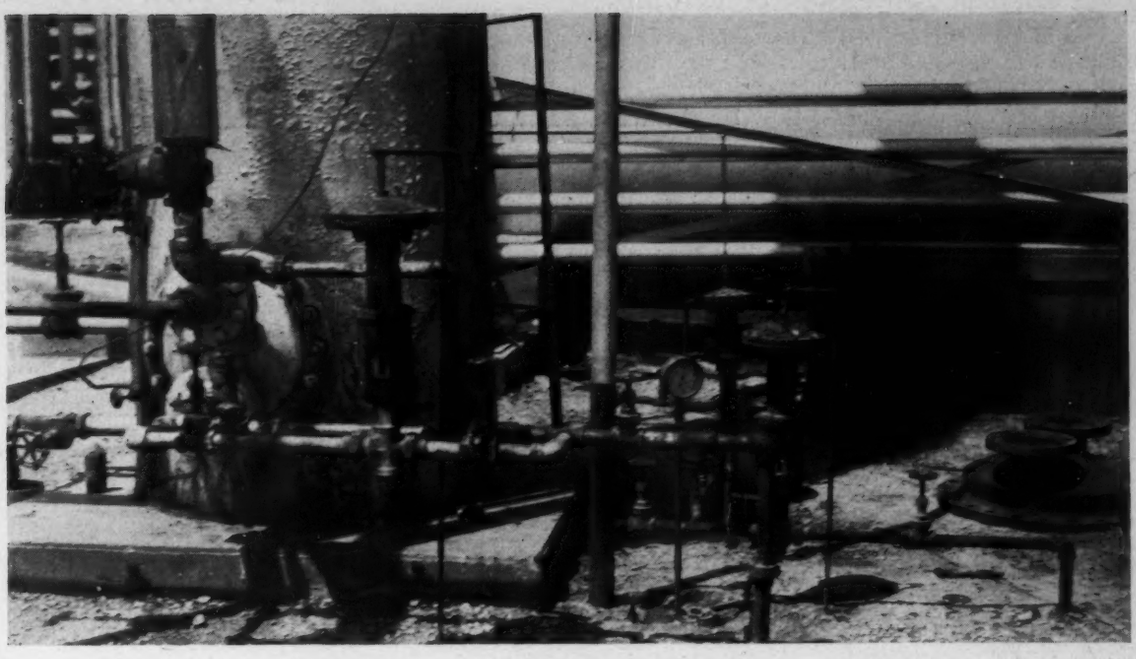
Suction lines leading to engines in J. E. Crosbie, Inc., gasoline plant at Fitts, Oklahoma.

Gasoline Plant in Fitts Pool Has Operating Problems

J. E. CROSBIE, INC., et al erected a gasoline plant in the Fitts pool, Oklahoma, soon after that area became a factor in the production of natural gasoline because of the large volume of gas produced with the oil. The plant consists of a distillation system with the necessary absorbers, and was designed to operate at low pressure from the wells without boosting. Shortly thereafter, because of the distance of a number of wells from the plant, it became necessary to put vacuum on the gathering system, and four engines were installed.

Practically all major units of equipment used had seen service in other fields, which required that it be reconditioned for use in this plant. The engines, for example, came from various dismantled plants. Before they were installed the power cylinders were sent to a machine shop where they were re-bored and new, pistons fitted. Main and crank bearings were removed and rebabbitted. Crank shafts and crank pins were found to be in good condition. Magnetos were reconditioned, new wiring installed and the unit given a general cleaning and repainted. The cost per engine for the complete overhaul, including new pistons and rings for the power cylinders, the compressor ends, magnetos and repainting was about $500.00 per twin unit. Some of the units were purchased from other operators at a fraction of the original cost. Coupled with the price paid for the engines and the overhaul expense, the total outlay per unit was very low.

When pits were excavated for concrete foundations for the engines, it was known that if a series of engine foundations were tied together, less concrete would be necessary than if placed upon individual blocks. By doing this, comparatively shallow pits were necessary, and the parts of the blocks between

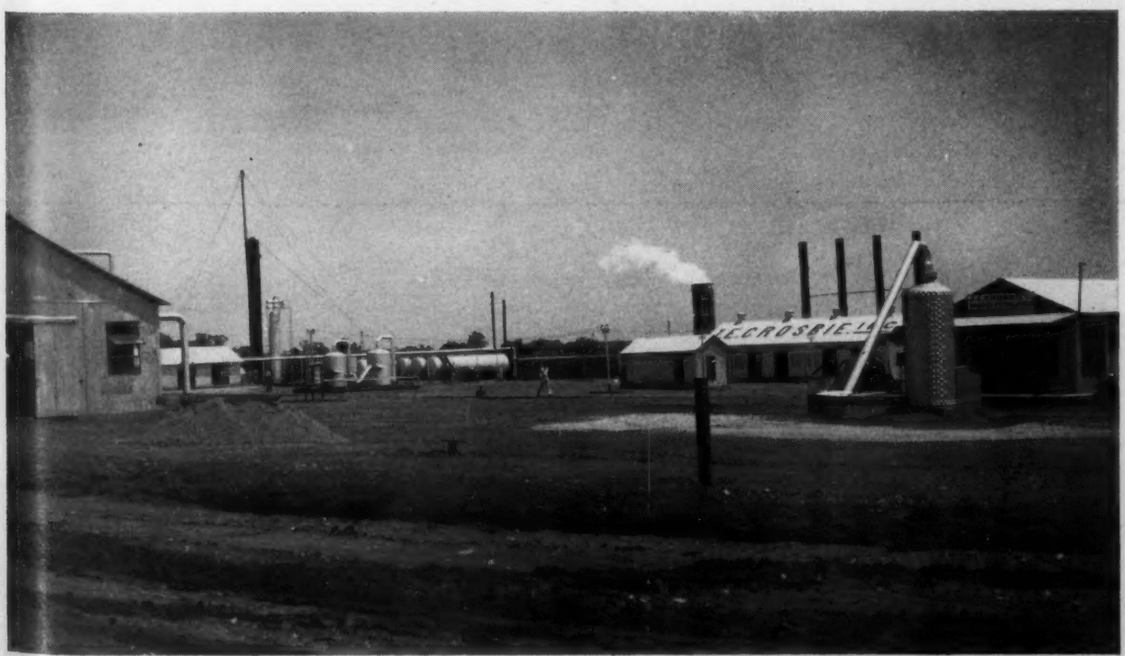


Three diaphragm friction free top valves on stabilizer.

engine settings formed the floor of the engine room. As the first installation of compressors included only four units, these were all set in this manner, but as it was expected that the field would increase greatly. requiring more horsepower to bring the gas in from the field, foundation reinforcing steel was left extending from the concrete so new blocks could be tied onto the first one. The next installation consisted of five twin engines which were installed in the same manner.

The most difficult feature in operating a plant at Fitts is the irregularity of flowing the wells. Wells which may be flowed for only a short time to obtain the allowable production are sometimes "kicked wide open" and the gas volume for the short period is much more than the gathering systems will handle. It appears that if the wells are fitted with flow beans they can be produced over a longer interval with a steady flow of gas from the traps, but paraffin difficulties begin to appear, which sometimes becomes so troublesome that bottom-hole pressure devices cannot be run inside the tubing. So, in order to get the job done as quickly as possible, some of the producers have dispensed with flow-beans and obtain their quota of oil by flowing at full head.

About 10,000,000 cubic feet are passed through the Fitts plant during 24 hours. Of this about 7,000,-000 cubic feet passes through the unit from eight o'clock in the morning until about five o'clock in the afternoon. The remainder is spread out irregularly for the other 13 hours of the operating day. The most noticeable load comes into the plant from about 11 o'clock in the morning until about 1 o'clock in the afternoon, when the plant is fully loaded, with the nine engines laboring to handle the excessive load. During the peak periods all the operators are waiting upon the engines to favor those mostly in



Looking northeast through yard of J. E. Crosbie, Inc., gasoline plant.

need, by pinching back on the intake to the compressors. When the period of small volume appears, part of the engines are shut down and those running are only pulling a light load.

Two factors are against flowing the wells against a back pressure sufficiently high that the gas can be processed under well pressure. When high pressures are placed upon the separators the gas remains in solution with the oil to a great extent, particularly the fractions desired in gasoline manufacture, and the yield falls rapidly. The second factor is the attitude of a large number of the producers who do not choose to cooperate with the gasoline plants, due to the relatively small income derived from the gas royalties, which is not considered of sufficient importance to justify added expense for equipment, or another man on the lease.

The gas produced from the majority of the wells which have been connected to the plant gathering system has a gasoline content of about 0.4 gallons per thousand cubic feet. The range of content varies from a low of 0.3 g.p.m. to about 0.83 g.p.m., with an average specific gravity of around .82. Some of the wells which are produced more regularly, have a much higher gasoline content, especially those located on the edge of the field where the production is not large and the pressures are relatively small.

The company has made connections to about 110 wells in the Fitts pool, making it neccessary to lay gathering lines all the way across the field. The vacuum, or gathering lines extend from the farthest west well, to the last one completed on the east edge of the pool. About 3½ miles of 16-inch pipe were laid as a main trunk gathering line, with 12-inch extending about ¾-mile on each end. The large pipe was equipped with demountable couplings on the east mile and a half, but was welded on the west side. The remainder of the gathering system, especially the 12-inch was also welded as it was laid. Laterals and trap connections were made up with threaded connections which may be broken down easily when it is necessary to change a hookup.

Out of the 10,000,000 cubic feet of gas passed through the plant, about 8,000 gallons of finished gasoline is manufactured. The raw product is stabilized and continuously through a standard fractionator to a grade of about 26/70. The product is comparatively sweet and requires a short contact with hypochlorite to condition it for the buyer. It passes in a straight line from the accumulator tank through the treating system to the plant storage where it is removed under pressure and loaded in tank trucks.

A simple effective loading device was constructed near the plant office. This consists of a line leading from the storage tank outlet header with a gate and flanged connection for attaching the flexible hose to the truck manifold. Pressure from the storage tanks forces the gasoline into the twin tanks mounted upon the truck and pressure is always maintained upon the truck when it is loaded.

Utilization of Petroleum Coke

(*Continued from page 281*)

In view of the possibility of deriving Vanadium and other rare metals from petroleum coke a spectrographic analysis of the ash from the above coke was carried out, giving the following results:

SPECTROGRAPHIC ANALYSIS OF PETROLEUM COKE ASH

High	Low	Present	Trace	Spectographic Trace	Not found
Iron Sodium	Calcium Barium Strontium Silica Tin Aluminum	Potassium Vanadium Boron Manganese	Magnesium Copper	Chromium Zinc Molybdenum Silver Cobalt Nickel Titinium	Antimony Beryllium Cadmium Gold Lithium

That the presence of rare metals in petroleum coke is not merely of academic interest is evidenced by the fact that a patent has been granted to Oberle[35] for recovering vanadium from petroleum hydrocarbons, in which petroleum coke is specifically mentioned. Baldeschwieler also possesses a patent for the recovery of vanadium[36]. It has even been stated[37] that sufficient vanadium occurs in the ash of certain petroleums, notably Mexican, to make it worth while collecting it from tanker vessels burning such a fuel for the subsequent recovery of its vanadium content.

To summarize, petroleum coke can be advantageously used for practically all the applications of coke derived from the destructive distillation of good quality coke. One of the few exceptions is that its friability precludes its use under conditions when it has to support a heavy load, as for instance in blast furnaces.

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